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TABLE OF INTERNATIONAL ATOMIC WEIGHTS (1942)

	<i>Symbol</i>	<i>At. Number</i>	<i>At. Weight</i>		<i>Symbol</i>	<i>At. Number</i>	<i>At. Weight</i>
Aluminum....	Al	13	26.97	Mercury.....	Hg	80	200.61
Antimony....	Sb	51	121.76	Molybdenum..	Mo	42	95.95
Argon.....	A	18	39.944	Neodymium...	Nd	60	144.27
Arsenic.....	As	33	74.91	Neon.....	Ne	10	20.183
Barium.....	Ba	56	137.36	Nickel.....	Ni	28	58.69
Beryllium....	Be	4	9.02	Nitrogen.....	N	7	14.008
Bismuth.....	Bi	83	209.00	Osmium.....	Os	76	190.2
Boron.....	B	5	9.82	Oxygen.....	O	8	16.0000
Bromine.....	Br	35	9.916	Palladium....	Pd	46	106.7
Cadmium....	Cd	48	112.41	Phosphorus...	P	15	30.978
Calcium.....	Ca	20	40.08	Platinum....	Pt	78	195.23
Carbon.....	C	6	12.010	Potassium....	K	19	39.096
Cerium.....	Ce	58	140.13	Praseodymium	Pr	59	140.92
Cesium.....	Cs	55	132.91	Radium.....	Ra	88	226.05
Chlorine.....	Cl	17	35.457	Radon (Nitron)	Rn	86	222
Chromium....	Cr	24	52.01	Rhenium.....	Re	75	186.31
Cobalt.....	Co	27	58.94	Rhodium....	Rh	45	102.91
Columbium....	Cb	41	93.1	Rubidium....	Rb	37	85.48
Copper.....	Cu	29	63.57	Ruthenium....	Ru	44	101.7
Dysprosium....	Dy	66	162.46	Samarium....	Sm	62	150.43
Erbium....	Er	68	167.2	Scandium....	Sc	21	45.10
Europium....	Eu	63	152.0	Selenium....	Se	34	78.96
Fluorine.....	F	9	19.00	Silicon.....	Si	14	28.06
Gadolinium....	Gd	64	156.9	Silver.....	Ag	47	107.880
Gallium.....	Ga	31	69.72	Sodium.....	Na	11	22.997
Germanium....	Ge	32	72.60	Strontium....	Sr	38	87.63
Gold.....	Au	79	197.2	Sulfur.....	S	16	32.06
Hafnium.....	Hf	72	178.6	Tantalum....	Ta	73	180.88
Helium.....	He	2	4.003	Tellurium....	Te	52	127.61
Holmium....	Ho	67	164.94	Terbium....	Tb	65	159.2
Hydrogen....	H	1	1.0080	Thallium....	Tl	81	204.39
Illinium....	Il	61	.	Thorium....	Th	90	232.12
Indium.....	In	49	114.76	Thulium....	Tm	69	169.4
Iodine.....	I	53	126.92	Tin.....	Sn	50	118.70
Iridium....	Ir	77	193.1	Titanium..	Ti	22	47.90
Iron.....	Fe	26	55.85	Tungsten....	W	74	183.92
Krypton.....	Kr	36	83.7	Uranium....	U	92	238.07
Lanthanum....	La	57	138.92	Vanadium....	V	23	50.95
Lead.....	Pb	82	207.22	Xenon.....	Xe	54	131.3
Lithium.....	Li	3	6.940	Ytterbium....	Yb	70	173.04
Lutecium....	Lu	71	174.99	Yttrium.....	Y	39	88.92
Magnesium....	Mg	12	24.32	Zinc.....	Zn	30	65.38
Manganese....	Mn	25	54.93	Zirconium....	Zr	40	91.22

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# SEMIMICRO QUALITATIVE ANALYSIS

*A Course in*  
**APPLIED CHEMICAL EQUILIBRIUM**

BY

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AND

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## PREFACE

The present-day instructor in qualitative analysis is often confronted with the problem of deciding between macro and semimicro procedures for use in his courses. The proponents of each system have their valid arguments for its adoption, and the choice frequently depends not only on the scientific and pedagogical merits of the system, but also on the degree to which it will fit into an existing order of things in a college. This latter problem may involve quantities such as space, existing equipment, and funds.

To the present user of macro qualitative procedures may we say, however, that the transition to the semimicro scheme is less painful than might be expected. The chemical principles being taught are naturally the same under both systems, leaving the teaching problem essentially unchanged. The chemicals used are practically identical for all qualitative schemes, macro or semimicro. As inspection of this book will show, relatively small amounts of new (and inexpensive) equipment are required to adopt the semimicro system. The average course in macro qualitative analysis can be shifted to a semimicro basis with a surprisingly small expenditure of time and money.

The present user of semimicro procedures, convinced of the desirability of the system, may find in this book certain simplifications of older procedures, together with entirely new sets of procedures, that will commend it to his attention.

A course in the theory and practice of qualitative analysis may be considered as a course in chemical equilibrium. We have endeavored at all points to integrate theory and practice by including chapters on basic theory, and by the inclusion of notes adjoining the laboratory procedures themselves, in which the application of the theory is pointed out. The

emphasis is on chemical equilibrium as applied to processes actually used. The omission of chapters on atomic structure, valence, ionic theory, colloids, and physico-chemical methods of analysis may condemn the book to some readers. We have felt, however, that some of this material could be presupposed from general chemistry courses, and that the remainder of it was not directly relevant to the immediate interest of teaching the fundamentals of inorganic chemical reactions through the medium of qualitative analysis, at least not in an elementary course.

The procedures given here were developed and used originally in mimeographed form for a one-semester course at the University of Rochester. The rapid students easily finished the general material on cations and anions, and were able to analyze various ferro and aluminum alloys. In a longer course, particularly involving students in the specialized scientific fields, the study of these special procedures could be greatly extended.

We wish to thank the members of the classes in Chemistry 12 at the University of Rochester for their assistance, knowingly or otherwise, in bringing these pages into a final coherent and workable form. Appreciation is also expressed to Dr. Paul W. Aradine of the Taylor Instrument Company for numerous suggestions regarding the manuscript.

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ROCHESTER, NEW YORK  
January 26, 1943.

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## CHAPTER I

### INTRODUCTION

#### **The Nature of Qualitative Analysis.**

Analytical chemistry is the science of taking apart the matter of the physical world. Quantitative analysis deals with finding the percentage of one or more particular constituents in an unknown mixture; qualitative analysis is concerned with discovering what constituents are present in the unknown mixture, without too much regard as to their quantity. Generally, a qualitative analysis must precede a quantitative analysis, since the selection of the proper quantitative method depends on a knowledge of all constituents present in the sample. From this viewpoint, qualitative analysis is the more fundamental branch of analytical chemistry.

Qualitative analysis may be made of both organic and inorganic substances. The qualitative analysis of organic compounds constitutes a special field in itself, the study of which is reserved until experience has been gained in elementary organic chemistry. The qualitative analysis of inorganic compounds, however, may be undertaken profitably with considerably less chemical background. Many of the reactions employed are encountered in general chemistry, together of course with many new ones. The reactions are combined and used in such sequence as to make possible the systematic separation and identification of the constituents of the unknown substance. The student thus reviews older material, learns new reactions, and obtains a working knowledge of the theory and practice of inorganic chemistry.

Quite apart from its value in teaching the theory and practice of inorganic reactions, qualitative analysis has a definite practical value. The fields are numerous in which applied

chemical analysis is used. In geology, for example, ores, rocks, and minerals are examined to detect the presence of certain constituents essential for their identification or economic valuation. In medicine, particularly pathological work, it is frequently necessary to analyze certain organs or tissues for traces of inorganic materials, for example, arsenic, lead, mercury, or cyanide poisons. Metals and alloys are frequently "typed" by dealers by making qualitative tests to determine the principal constituents. Qualitative tests for traces of inorganic impurities are often made on laboratory reagents, particularly when extremely accurate or critical work is involved. ✓

Beyond its value in teaching inorganic chemistry, and its practical value, qualitative analysis has a definite place as a cultural study in a program of liberal education. It teaches patience and careful manipulation, neatness and orderliness, self-reliance, and finally the art of making accurate observations and drawing from them the logical conclusions. The qualitative analysis scheme is a system of applied logic; positive and negative results are weighed, inclusions and exclusions made, and conclusions drawn. The entire principle of the scientific method is illustrated in the performance of a single qualitative analysis.

### **Macro, Micro, and Semimicro Analysis.**

In recent years the terms "macro," "micro," and "semimicro" have been applied in qualitative and quantitative chemical analysis to designate the scale on which operations are carried out. Macro qualitative analysis deals with relatively large quantities—volumes of from 10 to 100 milliliters; masses of from 10 to 500 milligrams. Micro analysis may deal with quantities one-tenth or one-hundredth as large as these; it requires special small apparatus, delicate manipulation, and carefully developed technique. Between the extremes of macro and micro analysis (the limits of which are by no means rigorously defined) lies the field of semimicro

analysis. It operates on an intermediate scale; the volumes of solution handled rarely exceed 10 milliliters, nor are they less than 0.2 or 0.3 milliliter. The masses handled may vary from 1 to 25 milligrams, occasionally more. The apparatus is borrowed from both the micro and macro techniques; also, there are certain new developments, especially adapted for semimicro work.

Historically, the development of the micro and semimicro technique dates from the researches of Emich and Pregl, early in the twentieth century. These investigators developed methods for the quantitative analysis of small amounts of organic compounds, devising the necessary small apparatus for performing the analyses. Much of the apparatus developed by these workers is used in semimicro work.

Micro qualitative analysis received impetus from the work of F. Feigl, who developed sensitive "spot tests" for inorganic (and organic) substances, employing sensitive organic reagents. These tests were carried out on a spot plate, using only a few drops of the unknown solution. As the reagents which were employed produced extremely pronounced colors, exceedingly small quantities of a substance could be readily detected.

The combination of these newer techniques with the older ones previously used in qualitative analysis has resulted in the development of the new field of semimicro qualitative analysis.

## CHAPTER II

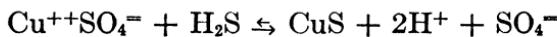
### CHEMICAL EQUILIBRIUM

#### **The Concept of Equilibrium.**

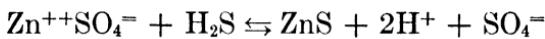
The term equilibrium has various shades of meaning, depending on whether it is used by the philosopher, psychologist, chemist, or physicist. In all its uses, however, the idea conveyed is one of coming into balance, of attaining a natural position of rest. The metaphysicists point out that the universe itself is coming to equilibrium, i.e., "running down." Thus the concept and specific nature of equilibrium processes are of fundamental importance in all natural science.

Used in a chemical sense, the term equilibrium implies a reversible reaction in which the interaction between two or more substances has proceeded as far as possible under the existing conditions and that the forward rate of reaction between the reactants is equal to the backward rate between the products (see p. 6). In other words, a stable condition has been reached. The position of equilibrium will depend upon the conditions of the reaction. Certain reactions will go quantitatively to completion in one direction; others may come to equilibrium with considerable amounts of all products and reactants present. In general, it is the former which are of greatest interest and importance in analytical work.

If hydrogen sulfide is passed into an aqueous solution of copper sulfate, all but traces of the copper are precipitated as copper sulfide. The reaction is quantitatively complete. In the following equation, the long arrow indicates that the equilibrium is far to the right as the expression is written. (This convention in writing equations will be followed throughout the text.)



On the other hand, if hydrogen sulfide is passed into a water solution of zinc sulfate, the precipitation of zinc sulfide is very incomplete. At the start of the reaction the solution is practically neutral, and under these conditions zinc sulfide precipitates. As the reaction proceeds, however, the acidity of the solution increases as the sulfide ion combines with zinc ion and the hydrogen ion is set free ( $\text{H}_2\text{SO}_4$  is highly dissociated). The increase in hydrogen ion concentration tends to reverse the reaction and even when the solution is saturated with hydrogen sulfide, an equilibrium is established with considerable zinc ion still in solution. While the copper sulfate reaction with hydrogen sulfide goes practically to completion, the zinc sulfate reaction is quite incomplete under the same conditions. This fact is indicated in the equation by using arrows of equal length.



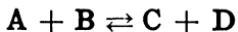
Zinc sulfide can be precipitated quantitatively in an alkaline solution (very low hydrogen ion concentration), or from a weakly acid solution, provided the hydrogen ion concentration is prevented from increasing by means of a buffer (see Chapter III, p. 17, and P 51).

Another factor which influences the position of equilibrium in a chemical reaction is the temperature, an increase of which usually causes the reaction to proceed in the direction in which heat is absorbed. For example, if heat is absorbed during the dissolving of a salt, increase in temperature will increase the solubility of the salt. The effect of another factor, the pressure, on an equilibrium may be predicted from the LeChatelier-Braun principle, namely, that if any one of the factors determining an equilibrium is altered, then the equilibrium itself will shift in such a direction as to annul the effect of the altering agent. The effect of pressure is used in treating solutions with hydrogen sulfide to secure a more complete reaction.

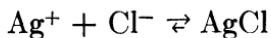
The concentration of the reactants also influences equilibrium; precipitations are made more complete by using a slight excess of precipitating agent.

### Reversible Reactions. The Equilibrium Constant.

In the reaction between **A** and **B** to yield products **C** and **D**, the products will react together to a certain extent, reforming **A** and **B**. Thus there are always two opposing processes in a chemical reaction; this is expressed by writing the equation for the reaction in the form:



When equilibrium has been reached we may still consider that the opposing processes are going on. In the case of a reaction which we call complete, as for example the reaction between silver and chloride ions, forming silver chloride, the amounts of silver and chloride ion in solution at equilibrium will be quite small; what is there will have been derived from the reverse reaction, the dissociation of silver chloride. The equation for this equilibrium process is written:



The existence of such a dynamic equilibrium has been demonstrated by means of radioactive indicators.\*

Chemical reactions attain the state of equilibrium with a definite rate, expressible as a number of mols reacting per second per unit volume. If the reaction is not too rapid, its rate may be measured; this subject is treated in courses in physical chemistry. In 1867 Guldberg and Waage published the results of studies on the rates of certain reactions. In brief, they found that in reactions of the type



\* Kolthoff and Yutzy, J. Am. Chem. Soc. 59, 1634 (1937).

the velocity of the forward reaction was proportional to the active masses (mols per unit volume) of the reactants **A** and **B**. Likewise, the velocity of the backward reaction is proportional to the concentrations of **C** and **D**.

Expressing these findings mathematically, we have:

$$\text{Velocity of forward reaction} = k_1 [A][B]$$

$$\text{Velocity of reverse reaction} = k_2 [C][D]$$

$k_1$  and  $k_2$  are the proportionality constants, and of course are not equal. The brackets [ ] indicate molar concentrations. The rates of the two opposing reactions are equal when equilibrium is reached, and we may write:

$$\text{Velocity of forward reaction} = \text{Velocity of reverse reaction}$$

$$k_1 [A][B] = k_2 [C][D]$$

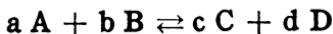
$$\frac{k_1}{k_2} = \frac{[C][D]}{[A][B]}$$

Division of a constant by a constant gives a constant, thus

$$K = \frac{[C][D]}{[A][B]}$$

This constant is called the equilibrium constant. It is a numerical quantity, expressing the extent to which a reaction is complete. The equilibrium constant is unique for each reaction, and remains essentially unchanged for any particular reaction at constant temperature. It is one of the most fundamental quantities which can be evaluated for a chemical reaction.

In the case of a reaction such as

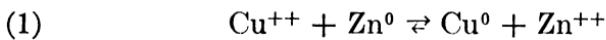


in which **a**, **b**, **c**, and **d** are integers, the equilibrium constant has the form:

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (\text{show why})$$

As before,  $[C]$ ,  $[D]$ ,  $[A]$ , and  $[B]$  are the molar concentrations of the substances in question.

If the equilibrium constant is very large, the reaction is one which is complete in the forward direction, while the reverse is true if the constant is small. The two following examples are cited:



$$K = \frac{[\text{Zn}^{++}]}{[\text{Cu}^{++}]} = 10^{37}$$



$$K = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} = 1.75 \times 10^{-5}$$

In the first case the reaction goes very far toward completion, while in the second case only a slight reaction takes place. (For methods of calculating these constants, see Chapters III and V.)

Although the value of the equilibrium constant may indicate that a reaction is theoretically complete, it nevertheless gives no indication as to the *rate* at which equilibrium is attained. The constant for the reaction



is of the order of  $10^{80}$ , yet the reaction proceeds so slowly that an immeasurably long time would be required for its completion. Only at sufficiently high temperatures does the rate increase. Sometimes a catalyst is used to hasten attainment of equilibrium, as for example the use of iron in the synthesis of ammonia from hydrogen and nitrogen. The position of equilibrium remains unchanged when a catalyst is used, despite the fact that the rate of reaction is altered.

As we shall see in the following chapters, the Law of Chemical Equilibrium developed here may be applied to a number

of chemical processes. It may be used in connection with ionization equilibria, for example, to treat the dissociation of weak electrolytes. It may be used in connection with oxidation-reduction equilibria, and finally in processes involving the equilibrium between a solid and dissolved phase, in which connection we shall study the Solubility Product Law.

## CHAPTER III

### APPLICATIONS OF THE LAW OF CHEMICAL EQUILIBRIUM. I. HOMOGENEOUS SYSTEMS

We shall now see how the Law of Chemical Equilibrium, developed in the preceding chapter, may be applied to numerous cases of homogeneous equilibrium.

Homogeneous systems are those consisting of one phase. Thus, reactions between ions in solution are homogeneous reactions, as are reactions in the gaseous phase.

#### Classification of Electrolytes.

Substances whose aqueous solutions conduct an electric current are termed electrolytes, and are commonly divided into two classes: (1) strong electrolytes and (2) weak electrolytes. The term electrolyte may apply to both inorganic and organic substances. Strong electrolytes are compounds that are completely ionized (dissociated) in aqueous solution, and readily conduct an electric current. Among such substances we find the inorganic acids, the soluble inorganic bases, and most salts. Examples of strong electrolytes would be: hydrochloric acid, HCl; nitric acid, HNO<sub>3</sub>; sodium hydroxide, NaOH; barium hydroxide, Ba(OH)<sub>2</sub>; potassium chloride, KCl; potassium acetate, KC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>; potassium cyanide, KCN. The Law of Chemical Equilibrium cannot be used to describe the behavior of strong electrolytes. Strong electrolytes in dilute solution are probably completely dissociated and hence no equilibrium can be established between ions and undissociated molecules. In addition, complications arise from the presence of the very large numbers of oppositely charged particles present per unit volume in such solutions. These

cations and anions, through their interactions without actually combining to form undissociated molecules, produce many anomalous effects.

The weak electrolytes are for the most part organic acids and bases, for example, acetic acid,  $C_2H_3O_2H$ ; benzoic acid,  $C_6H_5COOH$ ; aniline,  $C_6H_5NH_2$ ; together with a few inorganic compounds such as ammonium hydroxide,  $NH_4OH$ , and lead acetate,  $Pb(C_2H_3O_2)_2$ , which conduct an electric current only slightly. These compounds are only slightly dissociated in aqueous solution, usually a few percent or less. For a discussion of the fundamental differences between weak and strong electrolytes, particularly in regard to their electronic configurations, the student should consult a textbook of general chemistry. For our purposes we shall be interested only in their behavior in an aqueous solution.

### **Ionization Equilibria.**

In an aqueous solution of a weak electrolyte there are present the following ionic and molecular species: undissociated molecules of the weak electrolyte (present in large number), cations of the weak electrolyte, anions of the weak electrolyte, hydrogen ions derived from the dissociation of water, hydroxyl ions from the same source, and finally undissociated water molecules. As the quantities of hydrogen and hydroxyl ion obtained from the water are small compared with the other species present, we may disregard them.

Let us consider in detail the dissociation of a weak electrolyte such as acetic acid (conveniently abbreviated to  $HAc$ ) in a dilute aqueous solution. A solution of any desired strength\* of the acid in water may be prepared;  $0.1\text{ M}$  is a convenient strength to use. We may represent the dissociation of the acid by the equilibrium expression



\* See Appendix for definitions, p. 123.

The equilibrium constant for the process will be

$$K = \frac{[H^+][Ac^-]}{[HAc]}.$$

Modern experimental evidence points to the existence of the hydrated proton,  $H_3O^+$ , rather than the simple  $H^+$ , in an aqueous solution. A discussion of the evidence is beyond the scope of this book, and our derivations will suffer from no loss in applicability if we use  $H^+$  throughout the discussion, with the tacit understanding that we are perhaps oversimplifying the facts.

By suitable means the degree to which the acid has dissociated may be measured; in a 0.1 *M* solution it is found to be 1.32 percent. Therefore, the fraction (represented by the symbol  $\alpha$ ) of the acid dissociated is 0.0132. The concentration of hydrogen ion, in mols per liter, is

$$[H^+] = c\alpha = (0.1)(0.0132) = 0.00132$$

where  $c$  = total molar concentration of HAc. Since hydrogen ion and acetate ion are produced in equal amounts during the dissociation, the concentration of acetate ion will likewise be 0.00132 mols per liter. The concentration of undissociated acetic acid will be

$$\begin{aligned}[HAc] &= c(1 - \alpha) = 0.1(1 - 0.0132) \\ &= 0.099868\end{aligned}$$

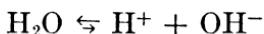
This is nearly 0.1, and the error introduced into our calculation will be negligible if we disregard the acid lost by dissociation.

Substituting these values into the expression for the equilibrium constant, we have:

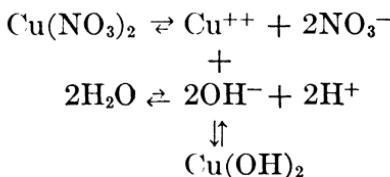
$$\begin{aligned}K &= \frac{[c\alpha][c\alpha]}{c[1 - \alpha]} = \frac{c^2\alpha^2}{c(1)} = c\alpha^2 \\ &= \frac{[0.00132][0.00132]}{0.1} = 1.75 \times 10^{-5}\end{aligned}$$

**K** is called the ionization constant of the acid. If we were to prepare another solution of acetic acid, say more dilute, there would be a greater percent of the acid ionized than in the previous case. (Why might you expect this to be true?) Nevertheless, if we measure  $\alpha$ , perform the calculations as above, finding  $[H^+]$  and  $[Ac^-]$ , and calculating the value of **K**, we will find that **K** has the same value as before. The ionization constant of any weak electrolyte, acid or base, remains essentially unchanged over a wide range of concentration, at constant temperature. The ionization constants for a large number of weak acids and bases have been determined; a partial list of these is given in the Appendix on p. 129.

Water is a very weak electrolyte which ionizes as follows:



In many reactions in which water is used as the solvent its ionization may be ignored because of the presence of other ions in much larger concentrations. In the reaction of silver nitrate with sodium chloride, for example, water may be regarded merely as an ionizing solvent, the presence of  $H^+$  and  $OH^-$  in the solution being unimportant. In a solution of sodium hydroxide in water, the hydroxide ion coming from the water is negligible in comparison with that coming from the sodium hydroxide. On the other hand, the fact that a solution of copper nitrate is acidic depends directly upon the reaction of the cupric ion with the hydroxyl ion furnished by the water:



The ionization constant for water is given by

$$\frac{[H^+][OH^-]}{[H_2O]} = K_i$$

Since the concentration of undissociated water,  $[\text{H}_2\text{O}]$ , is nearly constant at a value of 55.5 mols per liter, in most reactions taking place in dilute water solutions we may write:

$$[\text{H}^+] [\text{OH}^-] = \mathbf{K}_i [\text{H}_2\text{O}] = \mathbf{K}_w$$

$\mathbf{K}_w$  is known as the **ion product constant** for water. It has the approximate value of  $10^{-14}$  at room temperature.

The ion product expression for water tells us (1) that the concentrations of hydrogen ion and hydroxyl ion are inversely proportional to each other, and (2) that even in strongly acid solutions there is some hydroxyl ion present, and in strongly alkaline solutions a low concentration of hydrogen ion remains.

In pure water at room temperature,

$$[\text{H}^+] = [\text{OH}^-] = \sqrt{\mathbf{K}_w} = 10^{-7}$$

A solution of sodium hydroxide in which  $[\text{OH}^-] = 0.1 M$  would have a value of  $[\text{H}^+]$  of  $10^{-13} M$ .

$$[\text{H}^+] = \frac{\mathbf{K}_w}{[\text{OH}^-]} = \frac{10^{-14}}{10^{-1}} = 10^{-13}$$

Because of this relationship we can express the alkalinity as well as the acidity of solutions in terms of the same unit, namely, the hydrogen ion concentration. In order to express more conveniently the extremely wide ranges of hydrogen ion concentration encountered in water solutions, Sörensen in 1909 introduced the idea of using the negative logarithm of the hydrogen ion concentration instead of the hydrogen ion concentration itself, and used the symbol pH to designate this quantity.

$$\text{pH} = -\log [\text{H}^+] = \log \frac{1}{[\text{H}^+]}$$

In pure water,  $[\text{H}^+] = [\text{OH}^+] = 10^{-7}$ , or

$$\text{pH} = 7 = \text{pOH}$$

the quantity pOH being defined in a similar manner, i.e.,

$$\text{pOH} = -\log [\text{OH}^-] = \log \frac{1}{[\text{OH}^-]}$$

From the above, it follows that

$$\text{pH} + \text{pOH} = \text{p K}_w = 14$$

*Example:* What is the pH of a solution which is 0.00045 M in hydrogen ion? What is the pOH?

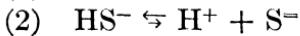
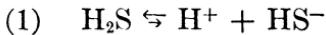
$$[\text{H}^+] = 4.5 \times 10^{-4}$$

$$\text{pH} = \log \frac{1}{4.5 \times 10^{-4}} = \log \frac{10^4}{4.5}$$

$$\text{pH} = 4 - \log 4.5 = 3.35$$

$$\text{pOH} = 14 - 3.35 = 10.65$$

Hydrogen sulfide is a weak acid of great importance in qualitative analysis, deserving special mention here. If hydrogen sulfide gas is bubbled into water until the solution is saturated with the gas, enough will have dissolved to form a 0.1 M solution of the acid H<sub>2</sub>S. As this acid possesses two ionizable hydrogens, it is called dibasic; we may represent the ionization of hydrogen sulfide as taking place in two steps:



For the first step of the dissociation,

$$\text{K}_1 = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = 9.1 \times 10^{-8}$$

However, since [H<sub>2</sub>S] in a saturated solution of the gas in water is 0.1 M,

$$\text{K}_1 = \frac{[\text{H}^+][\text{HS}^-]}{[0.1]} = 9.1 \times 10^{-8}$$

$$\text{K}_1 = [\text{H}^+][\text{HS}^-] = 9.1 \times 10^{-9}$$

For the second step of the dissociation,

$$\text{K}_2 = \frac{[\text{H}^+][\text{S}^=]}{[\text{HS}^-]} = 1 \times 10^{-15}$$

Multiplication of  $\mathbf{K}_1$  and  $\mathbf{K}_2$  yields a useful relation:

$$\mathbf{K}_1 \mathbf{K}_2 = \frac{[\mathbf{H}^+] [\mathbf{HS}^-] [\mathbf{H}^+] [\mathbf{S}^-]}{[\mathbf{HS}^-]}$$

$$= (9.1 \times 10^{-9})(1.0 \times 10^{-15})$$

$$\mathbf{K}_1 \mathbf{K}_2 = \mathbf{K}_{\mathbf{H}_2\mathbf{s}} = [\mathbf{H}^+]^2 [\mathbf{S}^-] = 9.1 \times 10^{-24}$$

Thus we have a relationship between sulfide ion concentration and hydrogen ion concentration in any saturated aqueous solution of hydrogen sulfide. The practical applications of this expression in predicting whether or not metallic sulfides will precipitate under certain conditions will become apparent later.

### PROBLEMS

(See Appendix for necessary data)

1. Calculate the ionization constant of HCN, a 0.1 *M* solution of which is 0.0084 percent ionized. What percent of the acid will be ionized in a 0.001 *M* solution?

*Ans.*  $7 \times 10^{-10}$ ; 0.084 percent.

2. A solution of an acid HX contains 30 grams of HX in 250 ml. The acid is 1.1 percent ionized; calculate the ionization constant of HX. Molecular weight of HX = 120.

3. A solution contains 20 percent by weight of acetic acid,  $\text{C}_2\text{H}_3\text{O}_2\text{H}$ . Calculate the hydrogen ion concentration of the solution.

4. The hydrogen ion concentration of a solution of acetic acid is  $10^{-4} \text{ M}$ . Calculate the molality of the acid. What is the pH of the solution?

5. How many grams of acetic acid,  $\text{C}_2\text{H}_3\text{O}_2\text{H}$ , are there in 10 ml. of the solution in problem (4)?

6. The ionization constant of a base BOH is  $10^{-8}$ . Calculate (a) the  $(\text{OH}^-)$  in a 0.01 *M* solution of the base; (b) the fraction ionized in the same solution. *Ans.* (b) 0.1 percent.

7. A solution contains 0.85 g. of ammonia,  $\text{NH}_3$ , per liter. Calculate the  $(\text{OH}^-)$  of the solution; the pOH, the pH.

8. Calculate the concentration of sulfide ion in a saturated aqueous solution of hydrogen sulfide which is 0.001 *M* in hydrogen ion; 0.3 *M* in hydrogen ion.

9. Calculate the sulfide ion concentration in a saturated aqueous solution of hydrogen sulfide which is (a) 1 *M* in acetic acid; (b) 1 *M* in hydrochloric acid.

10. A solution is 0.01 *M* in hydrochloric acid; 0.003 *M* in sulfuric acid; 1 *M* in acetic acid. Calculate the total hydrogen ion concentration of the solution.

### The Common Ion Effect. Buffers.

We may express the ionization of acetic acid as follows:



As this is a dynamic equilibrium, addition of one of the products of the ionization should cause it to be shifted backwards. If acetate ion in the form of sodium acetate is added to the solution of acetic acid, this displacement of the equilibrium will occur. The equilibrium will be shifted to the left; the degree of ionization of the acid will be decreased. The ionization constant of acetic acid will of course not be altered by addition of the acetate ion—which here we call the “common ion,” i.e., it is possessed both by acetic acid and sodium acetate—and we may calculate the effect of the common ion on the dissociation of the acid. For example: What will be the hydrogen ion concentration in a 0.1 *M* solution of acetic acid which is also 1 *M* in sodium acetate?

$$K_{\text{HAc}} = \frac{[\text{H}^+][\text{Ac}^-]}{[\text{HAc}]} = 1.75 \times 10^{-5}$$

If there were no common ion, both  $[\text{H}^+]$  and  $[\text{Ac}^-]$  would be set equal to  $x$ ;  $[\text{HAc}]$  being given as 0.1, the value of  $[\text{H}^+]$ , and of  $[\text{Ac}^-]$ , would be  $1.3 \times 10^{-3} \text{ M}$ . (Show why.) However, in the presence of the common ion,  $[\text{H}^+]$  no longer is equal to  $[\text{Ac}^-]$ .  $[\text{Ac}^-]$  will be approximately 0.1 *M*,\* since the dissociation of the strong electrolyte sodium acetate yields one mol of sodium and one mol of acetate ion. Substituting, we now have:

$$K_{\text{HAc}} = \frac{x \cdot 1}{(0.1)} = 1.75 \times 10^{-5}$$

\* Actually slightly greater than 1 *M*, since acetate ion will also be present from the dissociation of the acetic acid. This is negligible in comparison with the concentration of acetate ion supplied by the sodium acetate.

Solving for  $x$ , we have

$$x = (0.1) (1.75 \times 10^{-5}) = 1.75 \times 10^{-6}$$

Thus,  $[\text{H}^+] = 1.75 \times 10^{-6}$ . Addition of the common ion has decreased the hydrogen ion concentration by a factor of one thousand.

Solutions of the type under consideration are called buffer solutions. A buffer solution is defined as a solution of a weak acid or a weak base and its salt, having the property of maintaining a constant hydrogen or hydroxyl ion concentration when diluted, or when small amounts of acid or base are added to it. Some common buffer solutions are acetic acid-acetate ion, and ammonium hydroxide-ammonium ion.

The mode of action of a buffer, for example, the acetic acid-acetate ion buffer, is as follows: if hydrogen ion in the form of a strong acid is added to the buffer solution, acetate ion combines with it, forming more acetic acid. As the acetic acid is only slightly dissociated, this small additional amount will not change the hydrogen ion concentration to any degree. If the solution had contained no acetate ions, the hydrogen ion concentration would have risen upon adding the strong acid. If a base is added to the buffer solution, the acetic acid reacts with it, forming water and an acetate. This consumes some of the acid, to be sure, but again, since the fraction of acid ionized is small, the net effect on the hydrogen ion concentration of the solution is small.

Similar reasoning may be applied to explain the action of the ammonium-hydroxide-ammonium ion buffer. Of course, buffers are limited as to the amount of acid or base they can "neutralize" before the hydrogen ion concentration changes. Addition of much hydrogen or hydroxyl ion to a buffer will cause its effect to be lost.

The fact that buffers permit the hydrogen ion concentration of a solution to be controlled rather closely makes them useful in both qualitative and quantitative separations. The separation of zinc sulfide from the elements of Group III in

the qualitative scheme is made possible by use of a buffer (see p. 76). Likewise the separation of barium and strontium chromates is made through use of a buffer (see p. 90).

## PROBLEMS

(See Appendix for necessary data)

1. Calculate the hydroxyl ion concentration in a 0.1 *M* solution of ammonium hydroxide which is (a) 0.1 *M* in ammonium chloride, and (b) 2 *M* in ammonium chloride.

*Ans.* (a)  $1.75 \times 10^{-5}$ ; (b)  $8.3 \times 10^{-7}$ .

2. One liter of 0.1 *M* acetic acid,  $C_2H_3O_2H$ , contains 100 g. of sodium acetate. Calculate (a) the hydrogen ion concentration of the solution; (b) the pH of the solution.

3. Five hundred ml. of a solution contains 4.25 g. of ammonia and 53 g. of ammonium chloride. Calculate (a) the hydroxyl ion concentration of the solution; (b) the pOH; (c) the pH.

4. What will be the change in hydrogen ion concentration caused by adding 10 ml. of 1 *M* hydrochloric acid to a liter of acetic acid-sodium acetate buffer, 0.1 *M* in acetic acid and 1 *M* in sodium acetate?

5. What will be the change in hydrogen ion concentration if 65 g. of potassium cyanide are added to 500 ml. of 1 *M* hydrocyanic acid, HCN?

6. What will be the pH of a solution containing 46 g. of formic acid,  $HCO_2H$ , and 200 g. of ammonium formate in 750 ml.?

## Complex Ions.

A second type of ionization equilibrium to which the Law of Mass Action applies is found in the dissociation of complex ions. Before entering a discussion of the nature of this equilibrium, a brief survey of the chemistry of complex ions will be given.

Complex ions in some form are familiar to most students of chemistry; the deep blue cupric ammonia complex, Turnbull's blue or Prussian blue, are complexes frequently encountered. Complex ions are formed by the interaction of a simple cation with neutral molecules, or with other ions. The first systematic study of complex compounds of this type was made by Alfred Werner late in the nineteenth century. He pictured certain metallic ions as having both primary and

secondary valences. The primary valences were used in forming the normal type of salt— $\text{CuSO}_4$ ,  $\text{CuCl}_2$ , etc., whereas the secondary valence was used to attach the neutral molecules, or other ions. Elements could have a variable secondary valence; the “coordination number” of an element was a measure of this. Copper reacted with four ammonia molecules to form  $\text{Cu}(\text{NH}_3)_4^{++}$ ; its coordination number was 4; silver, forming  $\text{Ag}(\text{NH}_3)_2^+$  had a coordination number of 2. Cobalt formed  $\text{Co}(\text{NH}_3)_6^{+++}$ ; its coordination number was 6. Both primary and secondary valences could operate simultaneously.

Werner’s “primary” valence we now recognize as electrovalence, involving the addition or removal of electrons from the outer electronic shells of the atom or ion. The “secondary” valence is a coordinate covalence; electrons are donated by the complex-forming molecule or ion to the central atom. Electrons are donated in pairs, and two, four, six, or even eight pairs can be donated to the central atom. The coordination number thus is the number of pairs of electrons donated when the complex ion is formed.

The donated electrons go to make up a stable group around the central atom. For example, the zinc atom has an electronic configuration of 2, 8, 18, 2. The two outer electrons may be removed, forming zinc ion,  $\text{Zn}^{++}$ , having the configuration 2, 8, 18, 0. This itself is a stable configuration. Zinc may form a complex ion with ammonia,  $\text{Zn}(\text{NH}_3)_4^{++}$ . The electronic configuration of the ammonia molecule is

..

H : N : H. Of the four pairs of electrons around the nitro-  
..  
H

gen, three are used in binding the hydrogens; the fourth is donated to the zinc ion. In all, four such pairs are donated from four molecules, making a stable ring of eight electrons around the central atom. The configuration of zinc in its ammonia complex thus becomes 2, 8, 18, 8.

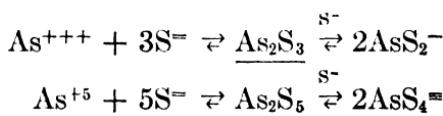
Depending on the element, the outer ring may contain four, eight, twelve, or sixteen electrons, made up as above by donation of electron pairs from ions or molecules. The elements forming complex ions are numerous; some common complexes encountered in qualitative analysis are the following:

1. *Ammonia Complexes.* Cadmium, cobalt, copper, nickel, silver, and zinc readily form complex ions with ammonia. The number of ammonia molecules attached to the central atom is twice the valence of the ion. Cobalt, having valences of +2 and +3, forms both  $\text{Co}(\text{NH}_3)_4^{++}$  and  $\text{Co}(\text{NH}_3)_6^{+++}$ , the latter form being the more stable; it is the one commonly obtained when cobalt solutions are treated with excess ammonia. This is one of the few occasions upon which cobalt shows a valence of +3; generally its valence is +2.

Derivatives of ammonia, such as hydroxylamine,  $\text{NH}_2\text{OH}$ , hydrazine,  $\text{NH}_2\text{NH}_2$ , and ethylene diamine,  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ , may also form complexes with the foregoing ions. Since each ethylene diamine molecule contains two nitrogen atoms, each with an unshared pair of electrons, the composition of a complex copper ion containing ethylene diamine, for example, would be  $\text{Cu}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2^{++}$ .

2. *Halide, Cyanide, Thiocyanate Complexes.* Antimony, arsenic, cadmium, cobalt, copper, iron, lead, mercury, nickel, silver, tin, and zinc form complexes with some or all of the above ions. Where variable valence of the metal ion is possible, the complex may form with both states. The various complexes of this type are listed in the table.

3. *Sulfide Complex Ions.* Antimony, arsenic, mercury, and tin (IV) react with sulfide ion,  $\text{S}^=$ , forming first the metallic sulfide, which then reacts further with excess sulfide ion forming soluble complex ions. The process may be represented as follows:



## COMPLEX IONS OF HALOGEN, CYANIDE, AND THIOCYANATE

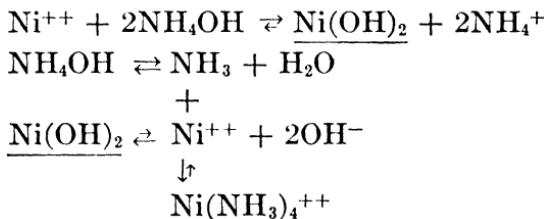
Element	Halogen complex (X = Cl <sup>-</sup> , Br <sup>-</sup> , I <sup>-</sup> )	Cyanide complex	Thiocyanate complex
Sb <sup>+++</sup> Sb <sup>+5</sup>	SbX <sub>4</sub> <sup>-</sup> SbX <sub>6</sub> <sup>-</sup>		
As <sup>+++</sup> As <sup>+5</sup>	AsX <sub>4</sub> <sup>-</sup> AsCl <sub>6</sub> <sup>-</sup>		
Cd <sup>++</sup>	CdX <sub>4</sub> <sup>-</sup>	Cd(CN) <sub>4</sub> <sup>-</sup>	Cd(CNS) <sub>4</sub> <sup>-</sup>
Co <sup>++</sup> Co <sup>+++</sup>	CoX <sub>4</sub> <sup>-</sup> CoX <sub>6</sub> <sup>=</sup>	Co(CN) <sub>6</sub> <sup>-4</sup> Co(CN) <sub>6</sub> <sup>=</sup>	Co(CNS) <sub>4</sub> <sup>-</sup> Co(CNS) <sub>6</sub> <sup>=</sup>
Cu <sup>+</sup> Cu <sup>++</sup>	CuCl <sub>2</sub> <sup>-</sup> CuCl <sub>3</sub> <sup>-</sup> CuCl <sub>4</sub> <sup>-</sup>	Cu(CN) <sub>2</sub> <sup>-</sup> Cu(CN) <sub>3</sub> <sup>-</sup> Cu(CN) <sub>4</sub> <sup>-</sup>	Cu(CNS) <sub>3</sub> <sup>-</sup>
Fe <sup>++</sup> Fe <sup>+++</sup>	FeCl <sub>6</sub> <sup>=</sup>	Fe(CN) <sub>6</sub> <sup>-4</sup> Fe(CN) <sub>6</sub> <sup>=</sup>	Fe(CNS) <sub>4</sub> <sup>-</sup>
Pb <sup>++</sup>	PbX <sub>3</sub> <sup>-</sup> PbX <sub>4</sub> <sup>-</sup>	Pb(CN) <sub>4</sub> <sup>-</sup>	
Hg <sup>++</sup>	HgX <sub>4</sub> <sup>-</sup>	Hg(CN) <sub>4</sub> <sup>-</sup>	Hg(CNS) <sub>4</sub> <sup>-</sup>
Ni <sup>++</sup>	NiX <sub>4</sub> <sup>-</sup>	Ni(CN) <sub>4</sub> <sup>-</sup>	Ni(CNS) <sub>4</sub> <sup>-</sup>
Ag <sup>+</sup>	AgCl <sub>2</sub> <sup>-</sup>	Ag(CN) <sub>2</sub> <sup>-</sup> Ag(CN) <sub>3</sub> <sup>-</sup>	Ag(CNS) <sub>2</sub> <sup>-</sup>
Sn <sup>++</sup> Sn <sup>++++</sup>	SnX <sub>4</sub> <sup>-</sup> SnX <sub>6</sub> <sup>-</sup>		
Zn <sup>++</sup>	ZnX <sub>4</sub> <sup>-</sup>	Zn(CN) <sub>4</sub> <sup>-</sup>	Zn(CNS) <sub>4</sub> <sup>-</sup>

The existence of most of the above complex ions in aqueous solution is fairly well established. The composition of certain complexes, for example, the ferric thiocyanate complex, remains unsettled. Where omissions have been made in the table, adequate evidence for the existence of the ions was lacking.

The importance of these complex ions, and a detailed description of their properties, is found on p. 65, note 1.

4. *Organic Ions*—such as oxalate, tartrate, succinate, form complexes with various metallic ions such as antimony, copper, iron, but these are not encountered in the scheme of qualitative analyses presented here.

The formation of a complex ion is favored by an excess of the complex-forming ion or molecule. Thus, silver ion forms silver chloride when treated with a moderate amount of chloride ion; a large excess of chloride ion causes the precipitate to dissolve, forming  $\text{AgCl}_2^-$ . A small amount of ammonium hydroxide added to a solution of nickel ion precipitates first nickel hydroxide; excess of ammonium hydroxide (which always contains free ammonia) causes the nickel ammonia complex to form, thereby dissolving the nickel hydroxide precipitate. The latter process may be represented:



Any reagent or treatment which removes the complex-forming ion or molecule from the equilibrium tends to cause decomposition of the complex ion. Thus, in the above case, an acid would decompose the complex ion, since ammonia would be removed from the equilibrium



by the reaction



### The Instability Constant.

A salt such as  $\text{Cu}(\text{NH}_3)_4\text{SO}_4$  or  $\text{K}_2\text{HgI}_4$ , etc., is a strong electrolyte, and in aqueous solution dissociates almost completely into anion and cation. A 0.1 *M* solution of the first

salt would produce 0.1 mol of  $\text{Cu}(\text{NH}_3)_4^{++}$  and 0.1 mol of  $\text{SO}_4^-$ , per liter.

Further dissociation of the complex ion may occur; it may dissociate into its simpler components to a very slight extent. Thus, in the case of the copper-ammonia complex:



The process is a reversible one, and an equilibrium is established to which the Law of Mass Action may be applied. The equilibrium constant for this particular case would be

$$K_{\text{inst.}} = \frac{[\text{Cu}^{++}][\text{NH}_3]^4}{[\text{Cu}(\text{NH}_3)_4^{++}]}$$

The constant indicates the extent of dissociation of the complex; it is usually called the "instability constant."

The degree of dissociation of the various complex ions may be measured, and from this their instability constants may be calculated. For example, the ion  $\text{Ag}(\text{NH}_3)_2^+$  is 1.2 percent ionized in a 0.1 M solution of the salt  $\text{Ag}(\text{NH}_3)_2\text{Cl}$ . The instability constant is

$$K_{\text{inst.}} = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]}$$

$$[\text{Ag}^+] = c\alpha = (0.1)(0.012) = 0.0012$$

$$[\text{NH}_3] = 2[\text{Ag}^+] = 2c\alpha = 0.0024$$

$$[\text{Ag}(\text{NH}_3)^+] = 0.1^*$$

$$K_{\text{inst.}} = \frac{[0.0024]^2 [0.0012]}{[0.1]}$$

$$= 6.9 \times 10^{-8}$$

\* Less a small amount, 0.0012, which has dissociated, but which may be neglected without materially affecting the accuracy of the calculation.

## PROBLEMS

(See Appendix for necessary data)

1. Calculate the cadmium ion concentration in (a) a 1 M solution of  $\text{Cd}(\text{NH}_3)_4^{++}$ ; (b) a 0.001 M solution of  $\text{Cd}(\text{NH}_3)_4^{++}$ .

*Ans.* (a)  $1.31 \times 10^{-2}$ ; (b)  $3.3 \times 10^{-3}$ .

2. Calculate the degree of dissociation and the percentage ionized of  $\text{Cu}(\text{NH}_3)_4^{++}$  in a 0.01  $M$  solution.

3. A solution contains 5.0 g. of  $\text{Ag}(\text{NH}_3)_2\text{Cl}$  in 300 ml. Calculate (a) the silver ion concentration of the solution; (b) the milligrams of silver ion,  $\text{Ag}^+$ , in the 300 ml.

4. In which solution will the concentration of free copper ion be greater, 0.1  $M$   $\text{Cu}(\text{NH}_3)_4\text{SO}_4$  or 0.1  $M$   $\text{K}_2\text{Cu}(\text{CN})_3$ ?

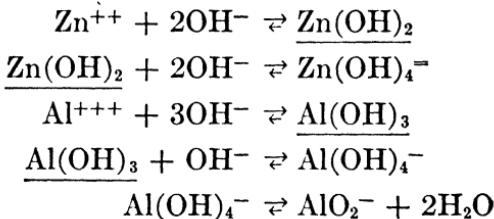
5. What will be the change in nickel ion concentration upon making a 0.1  $M$  solution of  $\text{Ni}(\text{NH}_3)_4^{++}$  0.5  $M$  in ammonia?

6. Calculate the instability constant for  $\text{Hg}(\text{CNS})_4^-$ , a 1.3  $M$  solution of which is 0.00106 percent ionized.

### Hydroxide Complex Ions. Amphotерism.

If the hydroxides of zinc, aluminum, beryllium, chromium, copper, tin, or antimony (arsenic might also be included formally in the list) are precipitated with a strong base such as sodium or potassium hydroxide, the addition of excess base over that required for complete precipitation will cause the hydroxides partly to redissolve. If a sufficient excess is added, the hydroxides may be redissolved completely. At the present time there are two explanations for this behavior.

1. *Formation of Hydroxide Complex Ions.* This theory postulates the following mechanism for the precipitation and redissolving of the hydroxides; using zinc and aluminum hydroxides as examples:



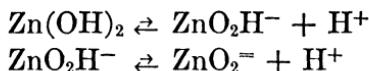
The formal resemblance between ions of this type and the halide complexes, for example, is apparent. The evidence for the compounds written above is not entirely conclusive, although in certain cases the theory of hydroxide complex ions fits observed experimental facts very well.

2. *Amphoterism.* The theory of amphotericism also endeavors to explain the behavior of hydroxides which dissolve in an excess of hydroxyl ions. It considers that the hydroxides ionize in two ways:

(a) as bases, e.g.,



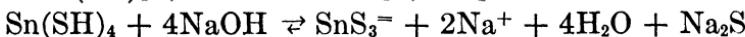
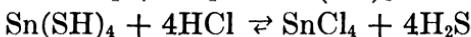
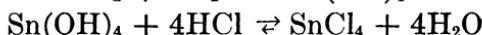
(b) as acids, e.g.,



In the case of a fairly basic hydroxide, such as  $\text{Be}(\text{OH})_2$ , the ionization will be primarily of the type (a). (Even more basic hydroxides, such as  $\text{Ca}(\text{OH})_2$ , ionize entirely in accord with (a); they are not detectably amphoteric.) A more "acidic" hydroxide, such as  $\text{Sb}(\text{OH})_3$ , will ionize primarily in accord with (b). In the former case, a strong base is necessary to redissolve the hydroxide, i.e., to bring forth its acid character. In the latter case, a weak base is sufficient.

These hydroxides dissolve in both acids and bases, hence the term "amphoteric" is applied to them.

Salts may also be amphoteric; the oxides and sulfides of some of the above elements show this property. For example,  $\text{SnO}_2$  dissolves in hydrochloric acid (concentrated) as well as in sodium hydroxide, or sodium sulfide. We may write equations expressing a probable mechanism for these processes, all of which take place in the presence of water.



The reactions are written in this manner to show the similarity in properties of compounds in which oxygen is replaced by sulfur. The behavior of arsenic, antimony, tin, and mercury sulfides of the above type is of greatest importance, and is used as a basis for separating these elements from others in Group II (see p. 65).

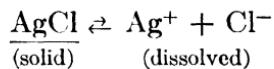
## CHAPTER IV

### APPLICATIONS OF THE LAW OF CHEMICAL EQUILIBRIUM. II. HETEROGENEOUS PROCESSES

#### The Equilibrium Between Solid and Dissolved Phase. Solubility Product.

If a large amount of some insoluble salt such as silver chloride is placed in water, the temperature maintained constant, and the solution agitated for several days, a definite amount of the salt will dissolve. Additional time spent in attempting to dissolve more of the salt will be of no avail. The amount dissolving will be independent of the quantity of solid salt originally taken, provided more than enough was taken to saturate the solution. As originally specified, the salt chosen was to be slightly soluble, so that even in a saturated solution, only a small amount will have dissolved.

An expression may be written to represent the dissolving process:



To this process we may apply the Law of Chemical Equilibrium. The equilibrium constant will be:

$$K_{\text{equil.}} = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]}$$

The solid phase, AgCl, is generally present in excess in any saturated solution of silver chloride. Since the amount dissolving is independent of the amount of solid present, provided enough is present to saturate the solution, and since in any case the concentration of a solid (g./cc.) is constant, we

may disregard this part of the equilibrium expression. Thus simplified, it reads:

$$K_{\text{equil.}} = \frac{[\text{Ag}^+][\text{Cl}^-]}{\text{some constant factor}} = S_{\text{AgCl}} = [\text{Ag}^+][\text{Cl}^-]$$

$S_{\text{AgCl}}$  is the **Solubility Product** of the silver chloride.

Stated in words, the solubility product means simply that the product of the ion concentrations in a saturated solution of a slightly soluble salt is constant. Thus, a saturated solution is one in which the product of the ionic concentrations (hereafter called "ion product") equals the solubility product. In an unsaturated solution the ion product is less than the solubility product; solid phase will dissolve until the ion product and the solubility product are equal. In a supersaturated solution the ion product exceeds the solubility product, and in such a case precipitation of solid phase will take place until the concentrations have been reduced to a point at which the ion product again equals the solubility product.

A solubility product may be calculated for any insoluble salt. Some typical salts for which this may be done are: the silver halides, barium and lead sulfates, many carbonates, oxalates, chromates, phosphates, hydroxides, and sulfides. Salts which are markedly soluble in water—sodium, potassium, and ammonium salts; metallic chlorides, nitrates, and sulfates, etc.—cannot be treated by the solubility product principle. Values of the solubility product for several salts are listed in the Appendix.

To calculate the solubility product of an insoluble salt, we must first find its molar solubility in water.

*Example:* Let us calculate the solubility products of two typical insoluble salts, (1) silver thiocyanate,  $\text{AgCNS}$ , and (2) silver chromate,  $\text{Ag}_2\text{CrO}_4$ .

1. The solubility of  $\text{AgCNS}$  is 0.000177 gram per liter of water at  $25^\circ \text{C}$ . As the molecular weight of  $\text{AgCNS}$  is approximately 166,

this corresponds to a solubility of  $\frac{177 \times 10^{-6}}{166} = 1.07 \times 10^{-6}$  mol per liter. Upon dissolving, each mol of  $\text{AgCNS}$  yields 1 mol of  $\text{Ag}^+$  and 1 mol of  $\text{CNS}^-$ ; hence,  $(\text{Ag}^+) = (\text{CNS}^-) = 1.07 \times 10^{-6}$ . The solubility product expression for  $\text{AgCNS}$  is

$$S_{\text{AgCNS}} = [\text{Ag}^+][\text{CNS}^-]$$

Substituting the molar concentrations of  $[\text{Ag}^+]$  and  $[\text{CNS}^-]$ , we have

$$\begin{aligned} S_{\text{AgCNS}} &= (1.07 \times 10^{-6})(1.07 \times 10^{-6}) \\ &= 1.1 \times 10^{-12} \end{aligned}$$

2. The solubility of silver chromate,  $\text{Ag}_2\text{CrO}_4$ , is 0.0435 gram per liter of water at  $25^\circ \text{C}$ . Since the molecular weight of the salt is 332, the molar solubility is  $\frac{435 \times 10^{-4}}{332} = 1.31 \times 10^{-4}$ . One mol of the salt upon dissolving gives 2 mols of  $\text{Ag}^+$  and 1 mol of  $\text{CrO}_4^-$ .

If we let

$$x = [\text{CrO}_4^-] \text{ (in mols per liter)}$$

Then

$$\begin{aligned} 2x &= [\text{Ag}^+] \text{ (in mols per liter)} \\ S_{\text{Ag}_2\text{CrO}_4} &= [\text{Ag}^+]^2[\text{CrO}_4^-] \\ &= (2x)^2(x) = 4x^3 \\ &= 4(1.31 \times 10^{-4})^3 \\ &= 9 \times 10^{-12} \end{aligned}$$

### Application to the Precipitation of Metallic Sulfides.

A large number of separations in systematic qualitative analysis are based on the precipitation of metallic sulfides. Three factors are of importance in the theory of these precipitations.

1. *Control of the hydrogen ion concentration.* Considering the equilibrium

$$[\text{H}]^2 [\text{S}^-] = 9.1 \times 10^{-24}$$

it is seen that the sulfide ion concentration will decrease as the hydrogen ion concentration increases. By control of the latter, the value of  $(\text{S}^-)$  may be kept at such a low value that only sulfides of extremely small solubility product will precipitate. The elements which comprise Group II have such sulfides.

2. *Differences in solubility products of the metallic sulfides themselves.* The sulfides of the Group III elements, zinc, cobalt, nickel, manganese, and iron, are more soluble than those of Group II. Accordingly, a higher sulfide ion concentration is needed to precipitate these ions.

3. *The concentration of any given ion* is also of importance in ascertaining whether or not the sulfide of the ion will precipitate. Enough must be present so that the product (concentration of ion)  $\times$  (concentration of sulfide ion) will exceed the solubility product of the sulfide in question.

The following example is given to show the working of these factors.

*Example:* Show why CuS may be precipitated from a solution containing 0.0010 g. of Cu<sup>++</sup> per 10 ml., and MnS not precipitated from the same solution if there is 0.0010 g. of Mn<sup>++</sup> present, and the [H<sup>+</sup>] is 0.3 M. What will be that maximum quantity of Mn<sup>++</sup> which may be retained in the solution under these conditions?

(a) Calculate the [S<sup>-</sup>] in the solution.

$$\begin{aligned} [\text{H}^+]^2[\text{S}^-] &= 9.1 \times 10^{-24} \\ [0.3]^2[\text{S}^-] &= 9.1 \times 10^{-24} \\ [\text{S}^-] &= 10^{-22} \end{aligned}$$

(b) Calculate the [Cu<sup>++</sup>] in the solution.

$$\begin{aligned} [\text{Cu}^{++}] &= 0.1 \text{ gram per liter} \\ &= \frac{0.1}{63.6} = 1.57 \times 10^{-3} \text{ mol per liter} \end{aligned}$$

(c) Calculate the ion product, [Cu<sup>++</sup>][S<sup>-</sup>].

$$\begin{aligned} [\text{Cu}^{++}][\text{S}^-] &= (1.57 \times 10^{-3})(10^{-22}) \\ &= 1.57 \times 10^{-25} \end{aligned}$$

Since the solubility product of CuS is 10<sup>-42</sup>, the ion product exceeds the solubility product, and precipitation will occur.

(d) Calculate the [Mn<sup>++</sup>] in the solution.

$$\begin{aligned} [\text{Mn}^{++}] &= 0.1 \text{ gram per liter} \\ &= \frac{0.1}{55} = 1.8 \times 10^{-2} \text{ mol per liter} \end{aligned}$$

(e) Calculate the ion product, [Mn<sup>++</sup>][S<sup>-</sup>].

$$\begin{aligned} [\text{Mn}^{++}][\text{S}^-] &= (1.8 \times 10^{-2})(10^{-22}) \\ &= 1.8 \times 10^{-24} \end{aligned}$$

Since the solubility product of  $\text{MnS}$  is  $7 \times 10^{-16}$ , the ion product does not exceed the solubility product, and precipitation does not occur.

If the  $[\text{S}^-]$  is  $10^{-22}$ , then before  $\text{MnS}$  will precipitate from this solution, the  $[\text{Mn}^{++}]$  must be slightly greater than  $\frac{7 \times 10^{-16}}{10^{-22}} = 7 \times 10^6$  molar—an impossibly large concentration.

### The Common Ion Effect.

Silver chloride dissolves in water to a slight extent; for the equilibrium which is set up we may write



This is a dynamic (mobile) equilibrium; if we add  $\text{Cl}^-$  to the solution, the equilibrium will be displaced to the left. This will cause silver chloride to precipitate, the result being a decrease in the solubility of silver chloride in the solution containing chloride ions. Silver ion added to the solution would have a similar effect. Thus as in the case of an ionization equilibrium (see p. 17), the addition of a common ion to the equilibrium system causes the equilibrium to be shifted.

The magnitude of the effect may be calculated. The solubility product of  $\text{AgCl}$  is about  $10^{-10}$ . In a saturated solution of  $\text{AgCl}$  in water,  $[\text{Ag}^+] = [\text{Cl}^-] = \sqrt{10^{-10}} = 10^{-5}$  mols per liter. This is also the number of mols of dissolved silver chloride. What now will be the solubility of silver chloride in  $0.1 \text{ M}$  potassium chloride solution? Since potassium chloride is almost completely ionized, both  $[\text{K}^+]$  and  $[\text{Cl}^-]$  will have the value  $0.1 \text{ M}.$ \* The potassium ion has no effect upon the equilibrium. Substituting the concentration of chloride ion in the solubility product expression:

$$\begin{aligned} [\text{Ag}^+] [0.1] &= 10^{-10} \\ [\text{Ag}^+] &= 10^{-9} \text{ molar} \end{aligned}$$

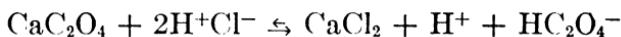
\* As seen before on p. 17, the concentration of chloride ion coming from the dissolved silver chloride is negligible in comparison with the concentration of the ion supplied by the potassium chloride.

Since each mol of dissolved silver represents 1 mol of dissolved silver chloride, the solubility of silver chloride will have become  $10^{-9}$  mols per liter. The 0.1 M potassium chloride has decreased the solubility by a factor of  $10^{-4}$ .

### Application of the Solubility Product Principle to the Dissolving of Precipitates.

In our discussion of applications of the solubility product principle it has been emphasized that, in order to produce a precipitate, the product of the concentration of the ions (ion product, I.P.) of the slightly soluble compound must exceed the solubility product of that compound. In other words, whenever  $I.P._{MX} > S_{MX}$ , a precipitate of MX is to be expected. Conversely, if for any reason the ion product becomes less than the solubility product, MX can be expected to dissolve. In seeking an explanation of why a compound dissolves upon the addition of a certain reagent, the student should ask himself the question: What changes in ionic concentrations take place, and in particular which ionic concentrations are decreased? Among the conditions which will cause a slightly soluble compound to dissolve are the following:

#### 1. The formation of a slightly ionized product.



$\text{HC}_2\text{O}_4^-$  is only weakly dissociated ( $K = 4.9 \times 10^{-5}$ ) and its formation decreases the concentration of  $\text{C}_2\text{O}_4^-$  to a point where  $[\text{Ca}^{++}][\text{C}_2\text{O}_4^-] < S_{\text{CaC}_2\text{O}_4}$  and hence  $\text{CaC}_2\text{O}_4$  dissolves.

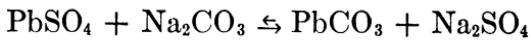
#### 2. The formation of a complex ion.



$$\frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2]^+} = 6.8 \times 10^{-8}$$

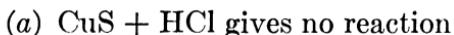
The  $[\text{Ag}^+]$  in a saturated solution of  $\text{AgCl}$  is reduced because of the formation of the complex ion. The  $I.P._{\text{AgCl}}$  becomes less than the  $S_{\text{AgCl}}$  and therefore  $\text{AgCl}$  dissolves.

3. *The formation of a less soluble compound.*



The  $S_{\text{PbCO}_3}$  is  $3.3 \times 10^{-14}$  and is less than the  $S_{\text{PbSO}_4}$ ,  $1.1 \times 10^{-8}$ , hence in this reaction the  $[\text{Pb}^{++}]$  is decreased by forming the less soluble  $\text{PbCO}_3$  and the  $[\text{SO}_4^{=}]$  goes into solution. Lead sulfate is quite insoluble in all acids but is decomposed readily and completely by boiling with sodium carbonate solution. Application is made of this type of reaction in the preparation of the solution for the anion analysis.

4. *Change of valence.*

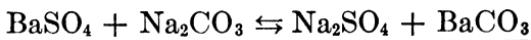


Copper sulfide is insoluble in hot dilute HCl because the concentration of sulfide ion is already so low in a saturated water solution of that compound that an equilibrium is quickly established between the trace of sulfide ion present and the hydrogen ion furnished by the HCl, and reaction ceases. On the other hand, if hot dilute  $\text{HNO}_3$  is used, the trace of sulfide ion is progressively removed by oxidation to free sulfur, the reverse reaction is prevented, and  $\text{CuS}$  dissolves completely.

**The Transposition of Salts.**

A method commonly used for bringing the anion constituent of certain insoluble salts into solution in order that they may be detected qualitatively consists of boiling the solid salt with a solution of sodium carbonate. This treatment converts the cation of the insoluble salt into a carbonate, also generally insoluble, and the sodium salt of the anion, which of course is soluble.

A typical case is the transposition of barium sulfate with sodium carbonate. The reaction is



Since the sodium sulfate is soluble, we shall be able to detect sulfate ion in the solution. The barium carbonate may be dissolved in acid and the cation also identified if desired.

The extent to which the reaction proceeds toward completion will determine how successful our tests will be. In the case of certain insoluble salts, such as the silver halides, the sodium carbonate treatment is not effective in bringing the anions into solution, while in other cases such as the above, enough salt is transposed to allow a good qualitative test for the anion to be made. The extent to which the reaction proceeds depends on the solubilities of the two solid phases involved; in this case on the solubility of  $\text{BaCO}_3$  and of  $\text{BaSO}_4$ .

The solubility products of the two salts are:

$$S_{\text{BaSO}_4} = [\text{Ba}^{++}][\text{SO}_4^{-}] = 1 \times 10^{-8}$$

$$S_{\text{BaCO}_3} = [\text{Ba}^{++}][\text{CO}_3^{-}] = 1 \times 10^{-10}$$

When equilibrium is attained, there can be but one ( $\text{Ba}^{++}$ ) in the solution, i.e., ( $\text{Ba}^{++}$ ) must satisfy both equations. Thus,

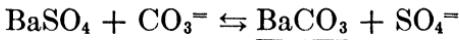
$$[\text{Ba}^{++}] = \frac{1 \times 10^{-8}}{[\text{SO}_4^{-}]} = \frac{1 \times 10^{-10}}{[\text{CO}_3^{-}]}$$

and

$$\frac{[\text{SO}_4^{-}]}{[\text{CO}_3^{-}]} = 0.02$$

This expression gives the ratio of sulfate concentration to carbonate concentration in solution when equilibrium has been reached. The following example will serve to illustrate the use of this expression.

How many grams of  $\text{SO}_4^{-}$  will be brought into solution by treating excess solid  $\text{BaSO}_4$  with 50 ml. of 1.5 M  $\text{Na}_2\text{CO}_3$  solution? The reaction will be:



At the start of the reaction,  $[\text{CO}_3^{-}] = 1.5 \text{ M}$ ;  $[\text{SO}_4^{-}] = 0$ . When equilibrium is reached,  $[\text{CO}_3^{-}] = (1.5 - x) \text{ M}$ ;  $[\text{SO}_4^{-}]$

$= x M$  (since for each  $x$  mols of  $\text{SO}_4^-$  going into solution,  $x$  mols of  $\text{CO}_3^-$  must precipitate out as  $\text{BaCO}_3$ ). Substituting in the expression for the equilibrium constant:

$$\frac{x}{1.5 - x} = 0.02$$

$$x = 0.029 \text{ mols per liter} = \text{SO}_4^-$$

The actual number of mols of  $\text{SO}_4^-$  in 50 ml. of solution will be

$$\frac{50}{1000} \times 0.029 = 0.00145 \text{ mols}$$

Since the molecular weight of  $\text{SO}_4^-$  is 96, the number of grams of  $\text{SO}_4^-$  in the 50 ml. of solution will be

$$0.00145 \times 96 = 0.139 \text{ g.}$$

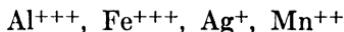
which is a quantity adequate for securing a conclusive test.

### PROBLEMS

(See Appendix for necessary data)

1. The solubility of silver bromide is  $1.1 \times 10^{-4}$  g. per liter at  $25^\circ \text{C}$ . Calculate the solubility product of silver bromide.  
*Ans.*  $3.4 \times 10^{-13}$ .
2. The solubility of barium sulfate is  $2.3 \times 10^{-3}$  gram per liter. Calculate the solubility product of barium sulfate.
3. The solubility of silver ferricyanide,  $\text{Ag}_3\text{Fe}(\text{CN})_6$ , is  $6.6 \times 10^{-5}$  g. per 100 ml. Calculate the solubility product of the salt.
4. The solubility product of silver phosphate,  $\text{Ag}_3\text{PO}_4$ , is  $1.56 \times 10^{-18}$ . Calculate the solubility of silver phosphate in terms of (a) mols per liter; (b) grams per liter.
5. How many grams of silver ion are in 10 ml. of a saturated solution of silver chloride?
6. What is the molar solubility of calcium oxalate,  $\text{CaC}_3\text{O}_4$ , in (a) water; (b) 1 M sodium oxalate?  
*Ans.* (a)  $4.3 \times 10^{-5}$ ; (b)  $1.8 \times 10^{-9}$ .
7. What is the barium ion concentration in a saturated solution of barium sulfate in water; in 0.1 M sulfuric acid; in 0.001 M sulfuric acid?
8. Calculate the milligrams of cupric ion remaining in solution after precipitation of 100 ml. of 0.1 M copper sulfate with excess hydrogen sulfide gas.

9. In what order would the following ions precipitate from a solution 0.01 *M* in metallic ion and 1 *M* in hydroxyl ion?



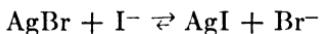
10. The solubility of calcium oxalate,  $\text{CaC}_2\text{O}_4$ , is  $4.3 \times 10^{-5}$  mol per liter. The solubility product of strontium oxalate,  $\text{SrC}_2\text{O}_4$ , is  $6.8 \times 10^{-8}$ . If a solution contains 0.3 mol of calcium ion per liter, and 26.28 g. of strontium ion per liter, calculate the oxalate ion concentration needed to precipitate the calcium but not the strontium.

11. Excess barium sulfate is boiled with 3 *N* sodium carbonate until equilibrium is reached. Calculate the sulfate ion concentration in milligrams per ml. of the final solution.

12. How many mols of solid barium sulfate will be converted into barium carbonate by 25 ml. of 1.5 *M* sodium carbonate solution?

13. Calculate the number of ml. of 3 *M* sodium carbonate solution needed to make a 10 percent conversion of a 2.53 g. sample of barium chromate into barium carbonate and sodium chromate.

14. Ten grams of solid silver bromide are treated with 100 ml. of 0.1 *M* potassium iodide solution, the reaction taking place being



Calculate (a) the equilibrium constant for the reaction; (b) the fraction of silver bromide converted into silver iodide by the treatment.

## CHAPTER V

### OXIDATION-REDUCTION REACTIONS

#### Definitions.

Modern physics has shown the atom to be a neutral body composed of a positive nucleus consisting of protons and neutrons, and surrounded by negative charges, the electrons. The chemical reactions of atoms involve these extra-nuclear electrons; they may be removed or added by other chemical reagents. The process whereby an atom (or an ion) loses an electron, or electrons, thereby gaining in positive charge, is called oxidation. The opposite process whereby an atom or ion gains electrons, also gaining in negative charge, is called reduction. The two processes are mutually dependent; a substance is oxidized only when simultaneously some other substance is reduced. The substance which oxidizes is called the oxidizing agent; the substance which reduces, the reducing agent. Sometimes the term "redox" is applied to oxidation-reduction processes for purposes of brevity.

#### Oxidation and Reduction, and the Periodic Table.

The strongest reducing agents are those chemical elements which, by loss of one electron, can assume the stable electronic configuration of an inert gas. Such elements as these are found in Group IA of the periodic table; they are Li, Na, K, Rb, and Cs. The elements of Group IB also lose one electron to form singly charged positive ions, but other considerations limit their reducing power. In their outermost electronic shell these elements of Group IA have a single electron, lost very readily with the formation of a singly charged positive ion. This ion possesses the rare gas configuration.

Elements having two electrons in their outermost shell (Group II elements such as Be, Mg, Ca, Sr, Ba) tend also to

lose electrons and become positive ions with a stable electronic configuration. The loss of two electrons by these elements proceeds with greater difficulty, however, than the corresponding loss of a single electron by the Group IA elements.

Thus we see that elements of both Group IA and IIA are strong reducing agents, easily oxidized, and consequently are difficult to reduce to the metallic state.

The elements which are the strongest oxidizing agents are those which need a single electron to complete their outermost electronic shell. Fluorine, chlorine, bromine, and iodine are such elements (Group VII<sub>B</sub>). Weaker oxidizing agents are the elements requiring two electrons to complete their outer shell. Such elements are oxygen, sulfur, selenium, and tellurium (Group VI<sub>B</sub>). Elements of both these groups, however, are strong oxidizing agents, easily reduced to the ionic state, and difficultly oxidizable to the element.

The majority of the chemical elements are of oxidizing and reducing power which is intermediate between the extremes noted above. It should be noted that ions, as well as the elements themselves, may act as oxidizing and reducing agents. In fact, more important examples of oxidation and reduction in qualitative analysis are found to take place between ions than take place between elements in their zero valence (atomic) state.

### Strength of Oxidizing and Reducing Agents.

Oxidizing and reducing agents differ widely in the intensity of their action. Metallic lithium is the strongest known reducing agent, while fluorine is the strongest oxidizing agent. Between these extremes are many substances of intermediate strength, some of which are listed in the Appendix, Table IV.

The strength of an oxidizing or reducing agent depends on certain fundamental properties of the atom and ion of the element in question. For a discussion of these factors, which

are beyond the scope of this book, the student is referred elsewhere.\*

A quantitative expression for the strength of oxidizing and reducing agents in homogeneous or heterogeneous systems is given by the Nernst equation. In brief, the Nernst equation relates the oxidizing power of an oxidation-reduction system to certain known physical constants, and to the concentrations of oxidized and reduced material in the system. Assuming a satisfactory derivation of the law, it may be written:

$$E = E_0 + \frac{RT}{nF} \ln \frac{(\text{Ox})}{(\text{Red})}$$

The meanings of the symbols are as follows:

$E$  is the oxidation potential, measured in volts. The greater the oxidation potential, the stronger the system as an oxidizing agent.

$E_0$  is a constant, characteristic of each redox system. The following section describes a method for evaluating the constant for any particular system.

$R$  is the gas constant, 8.432 joules.

$T$  is the absolute temperature.

$n$  is the number of electrons transferred during the oxidation-reduction reaction.

$F$  is the Faraday, 96,500 coulombs.

$\ln$  indicates the logarithm to the base  $e$  (natural logarithm).  $(\text{Ox})$  designates the molar concentration of the oxidized form in the system.

$(\text{Red})$  designates the molar concentration of the reduced form in the system.

If we substitute the numerical values of the constants and multiply by the factor 2.303 which converts natural to Briggsian (common, base 10) logarithms, the Nernst equation becomes,

\* W. M. Latimer, "Oxidation Potentials," Chapter II, Prentice-Hall, Inc., New York, 1938.

at 25° C.:

$$E = E_0 + \frac{0.059}{n} \log \frac{(\text{Ox})}{(\text{Red})}$$

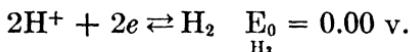
The Nernst equation is most commonly used in this form.

### Measurement of the Oxidation Potential.

Consider a silver wire (an electrode) dipped in a solution of silver nitrate, the concentration of which is 0.1 *M*. There will be a definite electrical potential established at the electrode; silver ions will tend to deposit on the metal and form metallic silver, while opposing this tendency will be a tendency on the part of the silver atoms to go into solution and become silver ions. The net result of these opposing effects is an electromotive force (emf) set up at the electrode-solution interface. A system such as this constitutes a *half-cell*, the potential of which we cannot measure directly. However, by combining this half-cell with another half-cell of known, or arbitrarily assigned, value, a complete cell is obtained, the emf of which can be measured.

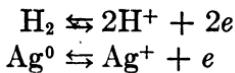
The potential of a cell may be measured by any device capable of measuring small emf's with accuracy. A potentiometer is the instrument usually selected. Upon connecting the two half-cells, a current will flow in the circuit, and a chemical reaction will take place at each electrode.

Obviously, it would be convenient if a standard half-cell were available, the potential of which was always known. Such a cell has been chosen, and is the hydrogen electrode. A hydrogen electrode consists of metallic platinum, specially treated, immersed in a solution whose  $[\text{H}^+]$  is one molar, and having hydrogen gas at one atmosphere pressure bubbled over it. The half-cell reaction is

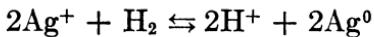


The potential of the hydrogen electrode has been assigned the value of 0.00 volt.

If we combine the hydrogen electrode with our silver electrode (half-cell), the two equilibria involved when chemical reaction commences will be:



When the half-cells are connected, electrons flow in the circuit, and the reaction takes place as follows:

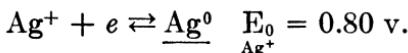


Since the total measured emf,  $E = E_1 - E_2$ , and  $E_1$ , the potential of the hydrogen electrode = 0.00 volt, then the measured emf will be the potential of the silver ion-silver metal system at the concentration and temperature in question.

### Applications of the Nernst Equation.

Let us consider two types of oxidation-reduction equilibria to which the Nernst equation may be applied.

1. Between Ions and Solid or Dissolved Substances.
- (a) Between ions and solid material, e.g.,



In this case,  $\text{Ag}^+$  is the oxidized form,  $\underline{\text{Ag}^0}$  the reduced form. The oxidation potential of the system will be

$$E = E_0 + \frac{0.059}{1} \log \frac{[\text{Ag}^+]}{[\underline{\text{Ag}^0}]}$$

For the establishment of a true equilibrium there must be an excess of  $\underline{\text{Ag}^0}$ , we may for any process in which silver ions and silver metal are involved, consider that  $[\underline{\text{Ag}^0}]$  is constant. The Nernst equation then becomes:

$$E = E_0 + 0.059 \log [\text{Ag}^+]$$

The constant  $E_0$  is evaluated by preparing a solution in which  $[\underline{\text{Ag}^+}]$  is known, and measuring its potential by combina-

tion with a hydrogen electrode, as previously described. Tables of  $E_0$  values are available (see Appendix); the value for  $\text{Ag}^0 - \text{Ag}^+$  is +0.80 volt. Thus the equation becomes

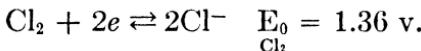
$$E = +0.80 + 0.059 \log [\text{Ag}^+]$$

*Example:* What will be the oxidation potential of a half-cell consisting of 0.001 M  $\text{Ag}^+$  in contact with excess silver metal?

$$\begin{aligned} E &= +0.80 + 0.059 \log [\text{Ag}^+] \\ &= +0.80 + 0.059 \log (10^{-3}) \\ &= +0.62 \text{ volt.} \end{aligned}$$

Thus we see that as the concentration of  $\text{Ag}^+$  in equilibrium with the electrode decreases, the electrode becomes more negative, i.e., more strongly reducing.

(b) Between ions and dissolved phase:



For this system the Nernst equation is

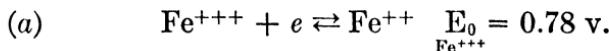
$$E = E_{\text{Cl}^-} + \frac{0.059}{n} \log \frac{[\text{Cl}_2]}{[\text{Cl}^-]^2}$$

The quantity  $[\text{Cl}_2]$  may be regarded as constant, since for the establishment of a true equilibrium between  $\text{Cl}_2$  and any concentration of  $\text{Cl}^-$ , the solution must be saturated with  $\text{Cl}_2$  gas. The equation then simplifies to:

$$\begin{aligned} E &= E_{\text{Cl}_2} + \frac{0.059}{2} \log \frac{1}{[\text{Cl}^-]^2} \\ &= E_{\text{Cl}_2} - \frac{0.059}{2} \log [\text{Cl}^-]^2 \end{aligned}$$

$E_{\text{Cl}_2}$  would be found as before, by measuring the emf of a half-cell having a known concentration of  $\text{Cl}^-$ , in combination with a hydrogen electrode. The value of  $E_{\text{Cl}_2}$  is +1.36 volts.

## 2. Between Ionic Species.



The oxidation potential of the ferrous-ferric system is given

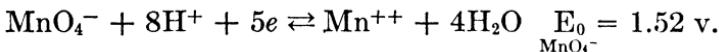
by:

$$E = E_{\text{Fe}^{++}} + \frac{0.059}{1} \log \frac{[\text{Fe}^{+++}]}{[\text{Fe}^{++}]}$$

Again,  $E_{\text{Fe}^{++}}$  is found by measuring the emf of a half-cell in which the ratio of  $\text{Fe}^{+++}$  to  $\text{Fe}^{++}$  is known. Note that the ratio  $\frac{[\text{Fe}^{++}]}{[\text{Fe}^{+++}]}$  is really the equilibrium constant for reaction (a). We may even rewrite the Nernst equation for this case as follows:

$$E = E_{\text{Fe}^{++}} - 0.059 \log K_{\text{equil.}}$$

(b) A more complicated oxidation-reduction system is the permanganate-manganous system.



$$E = E_{\text{MnO}_4^-} + \frac{0.059}{5} \log \frac{[\text{MnO}_4^-][\text{H}^+]^8}{[\text{Mn}^{++}][\text{H}_2\text{O}]^4}$$

As the equilibrium exists in aqueous solution,  $[\text{H}_2\text{O}]$  is negligibly small compared with the total amount of water present. Hence we regard it as constant, and the equation simplifies to

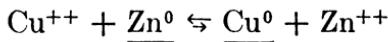
$$E = E_{\text{MnO}_4^-} + \frac{0.059}{5} \log \frac{[\text{MnO}_4^-][\text{H}^+]^8}{[\text{Mn}^{++}]}$$

### The Calculation of Equilibrium Constants.

We may obtain a picture of the chemical reaction between two systems of differing oxidation potential by means of the following analogy: One arm of a U tube, having a closed stopcock at the bottom, is half filled with water (Potential 1), while the other arm is completely filled (Potential 2). Upon opening the stopcock, water flows until the two levels are equal (Potential 1 = Potential 2). The position (equilibrium) finally held by the water level depends on the original difference in heights of the columns.

We may consider a chemical reaction between an oxidizing and a reducing agent as a process similar to the one described

above. Each system has its own potential; the extent to which the reaction proceeds, and in turn the equilibrium constant of the reaction, depends on the initial potentials of the separate systems. For example, let us consider the reaction



The two partial reactions in this case are

$$\text{Cu}^{++} + 2e \rightleftharpoons \underline{\text{Cu}^0} \quad E_{\text{Cu}^{++}}^0 = 0.34 \text{ v.}$$

$$\text{Zn}^{++} + 2e \rightleftharpoons \underline{\text{Zn}^0} \quad E_{\text{Zn}^{++}}^0 = -0.76 \text{ v.}$$

The potentials of the two partial (half-cell) reactions are:

$$E_1 = E_{\text{Cu}^{++}}^0 + \frac{0.059}{2} \log [\text{Cu}^{++}]$$

$$E_2 = E_{\text{Zn}^{++}}^0 + \frac{0.059}{2} \log [\text{Zn}^{++}]$$

At equilibrium,  $E_1 = E_2$ ,

$$E_{\text{Cu}^{++}}^0 + \frac{0.059}{2} \log [\text{Cu}^{++}] = E_{\text{Zn}^{++}}^0 + \frac{0.059}{2} \log [\text{Zn}^{++}]$$

Rearranging,

$$\begin{aligned} E_{\text{Cu}^{++}}^0 - E_{\text{Zn}^{++}}^0 &= \frac{0.059}{2} \log [\text{Zn}^{++}] - \frac{0.059}{2} \log [\text{Cu}^{++}] \\ &= \frac{0.059}{2} \log \frac{[\text{Zn}^{++}]}{[\text{Cu}^{++}]} \end{aligned}$$

Substituting the values of  $E_{\text{Cu}^{++}}^0$  and  $E_{\text{Zn}^{++}}^0$ , we have

$$+0.34 - (-0.76) = \frac{0.059}{2} \log \frac{[\text{Zn}^{++}]}{[\text{Cu}^{++}]}$$

$$\log \frac{[\text{Zn}^{++}]}{[\text{Cu}^{++}]} = 37$$

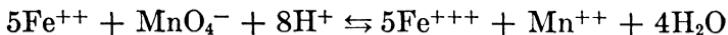
$$\frac{[\text{Zn}^{++}]}{[\text{Cu}^{++}]} = 10^{37} = \mathbf{K}_{\text{equil.}}$$

The magnitude of  $K_{\text{equil.}}$  indicates that the reaction is very nearly complete. If, for example,  $[\text{Cu}^{++}]$  had been  $0.1\text{ M}$  at the start of the reaction, then at equilibrium the  $[\text{Cu}^{++}]$  would be  $(0.1 - x)$ , while  $[\text{Zn}^{++}]$  would be  $(x)$ . Solving for  $x$ ,

$$\frac{x}{(0.1 - x)} = 10^{37}$$

$x$ , the  $[\text{Zn}^{++}]$  at equilibrium, is obviously very near to  $0.1\text{ M}$ . The amount of copper remaining in solution at equilibrium is vanishingly small.

As a more complicated exercise, let us calculate the equilibrium constant for the reaction



The emf's for the two partial reactions are given by:

$$E_1 = E_{0\text{ MnO}_4^-} + \frac{0.059}{5} \log \frac{[\text{MnO}_4^-][\text{H}^+]^8}{[\text{Mn}^{++}]}$$

$$E_2 = E_{0\text{ Fe}^{+++}} + \frac{0.059}{5} \log \frac{[\text{Fe}^{+++}]^5}{[\text{Fe}^{++}]^5}$$

(since we must write the partial reaction for the ferrous-ferric system as  $5\text{Fe}^{+++} + 5e \rightleftharpoons 5\text{Fe}^{++}$ ). At equilibrium the potentials of the two separate systems will be equal, thus

$$E_1 = E_2 \\ E_{0\text{ MnO}_4^-} + \frac{0.059}{5} \log \frac{[\text{MnO}_4^-][\text{H}^+]^8}{[\text{Mn}^{++}]} = E_{0\text{ Fe}^{+++}} + \frac{0.059}{5} \log \frac{[\text{Fe}^{+++}]^5}{[\text{Fe}^{++}]^5}$$

Rearranging terms,

$$E_{0\text{ MnO}_4^-} - E_{0\text{ Fe}^{+++}} = \frac{0.059}{5} \log \frac{[\text{Fe}^{+++}]^5}{[\text{Fe}^{++}]^5} - \frac{0.059}{5} \log \frac{[\text{MnO}_4^-][\text{H}^+]^8}{[\text{Mn}^{++}]} \\ = \frac{0.059}{5} \log \frac{[\text{Fe}^{+++}]^5 [\text{Mn}^{++}]}{[\text{Fe}^{++}]^5 [\text{MnO}_4^-][\text{H}^+]^8} \\ = \frac{0.059}{5} \log K_{\text{equil.}}$$

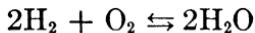
Substituting numerical values for  $E_0$ , we have

$$+1.52 - (+0.75) = 0.012 \log K_{\text{equil.}}$$

$$\log K_{\text{equil.}} = 64.2$$

$$K_{\text{equil.}} = 10^{64.2}$$

Again we have a reaction which is very nearly complete. The use of emf data in calculating whether or not a reaction may take place is of greatest importance in theoretical and applied chemistry. The equilibrium constant for any reaction may be calculated provided the oxidation potentials of the partial reactions are known. It should be noted, however, that the equilibrium constant merely tells *whether* a reaction is possible or not; it says nothing regarding the rate at which equilibrium is reached. As noted earlier in this book, the equilibrium constant for the reaction

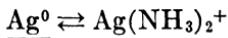


is very large, of the order of  $10^{80}$ . Nevertheless, the velocity of the reaction is so slow that years would be required for equilibrium to be reached.

### PROBLEMS

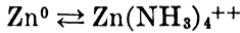
(See Appendix for necessary data)

1. What will be the oxidation potential of the  $\text{Cu}^0 \rightleftharpoons \text{Cu}^{++}$  system if  $[\text{Cu}^{++}]$  is (a)  $1\text{ M}$ ; (b)  $10^{-3}\text{ M}$ ; (c)  $10^{-20}\text{ M}$ ?  
*Ans.* (b)  $-0.43$  volt.
2. Calculate the oxidation potential of the  $\text{Ag}^0 \rightleftharpoons \text{Ag}^+$  system when the silver ion concentration is (a)  $0.5\text{ M}$ ; (b)  $3.2 \times 10^{-4}\text{ M}$ .
3. Calculate the oxidation potential of the system



if the concentration of the complex ion is  $0.1\text{ M}$ . (Hint: first calculate the silver ion concentration.)

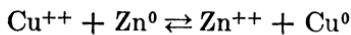
4. Calculate the oxidation potential of the system



if the solution is  $1\text{ M}$  in  $\text{Zn}(\text{NH}_3)_4\text{SO}_4$ .

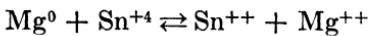
5. Which system will possess the greater oxidation potential,  $\underline{\text{Cu}^0} \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{++}$  (0.1  $M$ ), or  $\underline{\text{Cu}^0} \rightleftharpoons \text{Cu}(\text{CN})_3^-$  (0.1  $M$ )? [Note that copper has a valence of +1 in the ion  $\text{Cu}(\text{CN})_3^-$ .]

6. Calculate the equilibrium constant for the reaction

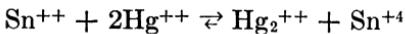


*Ans. K = 10^{37}*.

7. Calculate the equilibrium constant for the reaction



8. Calculate the equilibrium constant for the reaction



9. If in problem 6 the copper ion concentration had been 0.1  $M$  at the start of the reaction, what would have been its concentration at equilibrium? What would have been the concentration of zinc ion in solution at equilibrium?

10. Excess  $\underline{\text{Zn}^0}$  is added to a solution which is 0.1  $M$  in nickel ion. Calculate the concentrations of nickel, and of zinc ion in solution when equilibrium has been reached.

### GENERAL PROBLEMS

(See Appendix for necessary data)

1. Calculate the concentration of sulfide ion in a saturated aqueous solution of hydrogen sulfide which is also 0.1  $M$  in acetic acid and 1  $M$  in sodium acetate. Would zinc sulfide be precipitated from this solution if the zinc ion concentration were 0.01  $M$ ? If the solution were made 0.01  $M$  in cupric ion, would cupric sulfide precipitate?

2. Calculate the hydrogen ion concentration necessary to prevent precipitation of manganous sulfide from a solution containing 55 mg. of manganous ion per 25 ml.

3. The solubility product of magnesium hydroxide is  $3 \times 10^{-10}$ . A 0.1  $M$  solution of magnesium chloride is made 1  $M$  in ammonium chloride and 0.1  $M$  in ammonium hydroxide. Show whether or not magnesium hydroxide would precipitate from this solution.

4. If sufficient potassium iodide is added to a 0.4  $M$  solution of  $\text{KAg}(\text{CN})_2$  to make the iodide ion concentration 0.01  $M$ , will silver iodide precipitate?

5. Show whether or not cupric sulfide can be precipitated from a 0.001  $M$  solution of  $\text{Cu}(\text{NH}_3)_4\text{SO}_4$ , if the sulfide ion concentration is 0.05  $M$ .

6. What is the maximum number of mg. per ml. of aluminum ion that could remain in a liter of solution containing 5.0 g. of ammonium chloride and 10 g. of ammonium hydroxide?

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## PROCEDURES

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SEPARATION OF CATION CONSTITUENTS INTO GROUPS

Solution containing cation constituents. Add $\text{NH}_4\text{Cl}$ (P 11).	
<i>Precipitate:</i> Group I. $\text{AgCl}$ , $\text{Hg}_2\text{Cl}_2$ , $\text{PbCl}_2$ . Analyze by P 11-15.	<i>Precipitate:</i> Group II. $\text{CuS}$ , $\text{PbS}$ , $\text{CdS}$ , $\text{Bi}_2\text{S}_3$ , $\text{As}_2\text{S}_3$ , $\text{Sb}_2\text{S}_3$ , $\text{SnS}_2$ , $\text{HgS}$ . Treat with $\text{Na}_2\text{S}$ – $\text{NaOH}$ reagent (P 22).
	<i>Precipitate:</i> Add $\text{NH}_4\text{OH}$ , $\text{NH}_4\text{Cl}$ . Saturate with $\text{H}_2\text{S}$ gas (P 61).
	<i>Precipitate:</i> $\text{ZnS}$ . Confirm by P 52.
	<i>Precipitate:</i> Group III. $\text{CoS}$ , $\text{NiS}$ , $\text{MnS}$ , $\text{FeS}$ , $\text{Al}(\text{OH})_3$ , $\text{Cr}(\text{OH})_3$ . Treat with $\text{NaOH}$ – $\text{Na}_2\text{O}_2$ mix- ture (P 62).
<i>Residue:</i> Sub- group A. $\text{CuS}$ , $\text{PbS}$ , $\text{CdS}$ , $\text{Bi}_2\text{S}_3$ . Analyze by P 31-36.	<i>Solution:</i> Sub- group B as soluble salts. $\text{Na}_2\text{AsS}_4$ , $\text{Na}_2\text{SbS}_3$ , $\text{Na}_2\text{SnS}_3$ , $\text{Na}_2\text{HgS}_2$ . Analyze by P 41-49.
	<i>Precipitate:</i> $\text{Group IV}$ . $\text{MgCO}_3$ , $\text{CaCO}_3$ , $\text{BaCO}_3$ , $\text{SrCO}_3$ . Analyze by P 93-97.
	<i>Precipitate:</i> $\text{Group V}$ . $[\text{Mg}^{++}]$ , $\text{Na}^+$ , $\text{K}^+$ . Analyze by P 101-106.
	<i>Precipitate:</i> $\text{Group VI}$ . $\text{Al}_2\text{O}_3$ , $\text{NaAlO}_2$ , $\text{Na}_2\text{CrO}_4$ . Analyze by P 71-73.
	<i>Precipitate:</i> $\text{MnO}_2$ . Analyze by P 81-86.

## **PREPARATION OF UNKNOWNNS FOR ANALYSIS**

### **P 1. If the Unknown is a Solution, or a Water-Soluble Solid.**

If the unknown is a solution, test with litmus paper, neutralize with  $\text{HNO}_3$  or  $\text{NH}_4\text{OH}$  as required, and proceed directly with P 11. If the unknown can be dissolved in water, treat about 25 mg. of the substance with the minimum amount of hot water required to bring it into solution. Test with litmus, neutralize, and proceed with P 11.

### **P 2. If the Unknown is Water-Insoluble.**

If a solid unknown dissolves incompletely in water, add concentrated  $\text{HNO}_3$  to make the solution obtained in P 1 acid to litmus, then add several drops in excess. Boil several minutes, replacing the water which evaporates with  $\text{HNO}_3$ . If solution is complete, proceed as in P 1. If incomplete, add 10 drops of concentrated  $\text{HCl}$  and boil until dryness is nearly reached. Add 5 drops of  $\text{HCl}$  and repeat the evaporation. Take up the residue in 2 ml. of water, and proceed as in P 1.

### **P 3. If the Unknown is Insoluble in Aqua Regia.**

Filter the residue from P 2, reserving the solution. Mix the residue with about 0.2 g. of  $\text{Na}_2\text{CO}_3$  and 0.2 g. of  $\text{K}_2\text{CO}_3$ , place in a small nickel crucible and fuse. While the mass is still molten, dip into it a nichrome (or platinum) wire, then allow the melt to cool. The wire will "freeze" into the solidified mass, which may then be removed by lifting from the crucible after gentle reheating. Dissolve the mass in the minimum quantity of hot water, boiling if necessary. Mix the solution with that obtained at the beginning of this procedure, then proceed as in P 1.

### **P 4. If the Unknown is an Alloy.**

Treat 25 mg. (or larger amounts in the case of ferro-alloys and certain aluminum alloys) with 10 drops of  $\text{HNO}_3$ , heating

gently to assist in dissolving. If solution is incomplete, add several drops of concentrated  $\text{HNO}_3$ . If solution is then complete, proceed as in P 1. If not, treat the residue by P 2 and P 3 if necessary. Non-ferrous alloys generally respond to the treatment suggested, although frequently  $\text{SnO}_2$  fails to dissolve in the reagents prescribed.  $\text{HCl}$  is usually effective in dissolving  $\text{SnO}_2$ , also certain insoluble antimony and bismuth salts. Ferro-alloys generally contain silicon and carbon; these elements appear as insoluble material. Provision for detecting silicon is made in P 303. If the alloy contains a high percentage of aluminum, see p. 119, P 401.

## GROUP I

### P 11. Precipitation of the Silver Group.

Measure into a 100 mm. test tube 1 ml. of the unknown solution containing not more than 50 mg. of solids. If the solution is acid to litmus, neutralize with  $\text{NH}_4\text{OH}$ . If a precipitate forms, add 2 or 3 drops of  $\text{HNO}_3$  and heat until the precipitate is dissolved. (A black precipitate obtained upon neutralization with  $\text{NH}_4\text{OH}$  indicates the presence of mercurous ion. In this case begin with a fresh sample, omitting the neutralization.) Add  $\text{NH}_4\text{Cl}$  solution dropwise until precipitation is complete. Absence of a precipitate indicates that silver and mercurous ions are absent; the absence of lead is not certain.

Centrifuge any precipitate obtained; reserve the solution for P 21. Wash the precipitate with 0.5 ml. of 1 : 10 HCl, discarding the washings. To the precipitate add 1 ml. of water; heat to boiling; allow any precipitate remaining to settle. Treat the solution by P 12, the precipitate by P 13.

#### Notes

1. As the solution at this point may contain any or all of the cation constituents, it is entirely possible that some of these will precipitate as hydroxides or basic salts upon neutralization. This is true especially of bismuth and antimony, and of the elements of Group III. The precipitated salts will dissolve upon addition of the nitric acid, although heating may be necessary.

### P 12. Detection of Lead.

To the solution from P 11 add several drops of  $\text{K}_2\text{CrO}_4$  solution. Yellow precipitate:  $\text{PbCrO}_4$ .

### P 13. Separation of Silver and Mercury.

Treat the precipitate from P 11 with 1 ml. of  $\text{NH}_4\text{OH}$ , heating gently. Centrifuge; treat the solution by P 15. If a black residue remains, mercurous mercury is indicated.

**Notes**

1. By the action of  $\text{NH}_4\text{OH}$  (which contains some free  $\text{NH}_3$ ) on the mixed halides, silver chloride is dissolved as the complex ion  $\text{Ag}(\text{NH}_3)_2^+$ . The action of ammonium hydroxide on  $\text{Hg}_2\text{Cl}_2$  is somewhat complicated.\* The first step is thought to be:



The oxide formed in this step then reacts with the  $\text{NH}_4\text{Cl}$ :



The over-all reaction thus approximates the stoichiometry:



The black color of the precipitate obtained is due to the free mercury formed in the reaction.

2. If mercurous ion is found in Group I, the possibility of finding mercuric ion in Group II should not be overlooked, since the oxidation of mercurous to mercuric proceeds readily.

**P 14. Confirmation of Silver.**

Acidify the filtrate from P 12 with  $\text{HNO}_3$ . White precipitate:  $\text{AgCl}$ . If the test for silver is doubtful and a considerable amount of mercury has been found present, treat the black residue according to P 15.

**Notes**

1. Acidification of the solution containing  $\text{Ag}(\text{NH}_3)_2^+$  removes  $\text{NH}_3$  from the equilibrium  $\text{Ag}(\text{NH}_3)_2^+ \rightleftharpoons \text{Ag}^+ + 2\text{NH}_3$  by forming  $\text{NH}_4^+$ , hence  $\text{Ag}^+$  is liberated. Since there is chloride ion already present in the solution, a precipitate of  $\text{AgCl}$  forms immediately.

**P 15. Confirmation of Silver in the Presence of Large Amounts of Mercury.**

Add to the black residue a mixture of 1 ml. saturated bromine water and 0.5 ml.  $\text{HCl}$ . Stir thoroughly for a minute or two, then centrifuge. Wash the residue thoroughly with hot water, discarding the washings. Add 0.5 ml. 15 N  $\text{NH}_4\text{OH}$  to the precipitate, stir, and centrifuge. Acidify the solution with  $\text{HNO}_3$ . Pale yellow precipitate:  $\text{AgBr}$ .

\* H. Frecke and M. Snead, J. Am. Chem. Soc. 60, 518 (1938).

**Notes**

1. Treatment of the black residue with  $\text{Br}_2$  oxidizes the various forms of mercury in the precipitate to  $\text{HgBr}_2$ , which is water soluble, and converts into  $\text{AgBr}$  any silver salts which may have been retained by the precipitate. Hot water removes the  $\text{HgBr}_2$ . Any residue consists of  $\text{AgBr}$  and is dissolved by the concentrated  $\text{NH}_4\text{OH}$ .

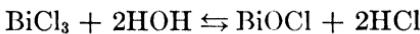
## GROUP II

### P 21. Precipitation of Copper-Tin Group.

Transfer the filtrate from P 11 to a small casserole and add 2 drops of 16 *N* HNO<sub>3</sub>. Evaporate to a thick paste but do not carry the evaporation to dryness. Add 3 drops of 12 *N* HCl and boil to decompose the HNO<sub>3</sub>. Add 0.5 ml. of H<sub>2</sub>O, transfer to a test tube, and neutralize the solution to litmus with NH<sub>4</sub>OH. Disregard any precipitate formed at this point. Acidify to litmus with HCl, then add 1 drop of 12 *N* HCl. Pass H<sub>2</sub>S into the cold solution for several minutes, then place the tube in a small flask or beaker of boiling water and continue passage of the gas for several minutes more. Dilute the solution to exactly 2 ml. and again saturate with H<sub>2</sub>S. Centrifuge and test the solution for completeness of precipitation. Wash the precipitate with two 0.5 ml. portions of water, discarding the washings. Treat the precipitate by P 22; the solution by P 50 and P 51.

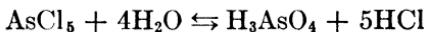
#### Notes

1. Evaporation with HNO<sub>3</sub> serves to oxidize arsenic, antimony, and tin to their higher valence states, in which form they are readily extracted during the subsequent NaOH-Na<sub>2</sub>S treatment. If bismuth or antimony is present, neutralization with NH<sub>4</sub>OH may cause precipitation of basic salts of these metals:

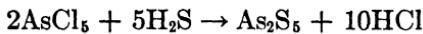


A similar reaction occurs with antimony. These salts are not readily redissolved upon acidification of the solution, but this need cause no concern, since treatment with H<sub>2</sub>S converts them completely to the corresponding sulfides.

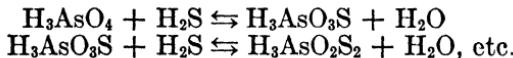
2. Complete precipitation of arsenic is insured by precipitation in hot concentrated solution at this point. In dilute acid solution this element would be present largely as the arsenate [AsO<sub>4</sub><sup>=</sup>] ion, in concentrated acid solution largely as the AsCl<sub>6</sub> or HAsCl<sub>6</sub>.



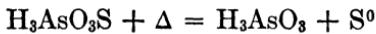
From a strongly acid solution, therefore, arsenic is precipitated rapidly and completely as  $\text{As}_2\text{S}_5$



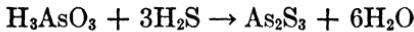
In dilute acid solution oxy-thio acids are formed by the replacement of oxygen by sulfur



These acids are unstable in hot solution,  $\text{H}_3\text{AsO}_2\text{S}$ , for example, decomposing to give arsenous acid and sulfur



The arsenous acid then reacts with  $\text{H}_2\text{S}$  to form  $\text{As}_2\text{S}_3$



The formation of the oxy-thio acids is a slow reaction, whereas the reaction of  $\text{AsCl}_5$  with  $\text{H}_2\text{S}$  is a rapid one. The solution is therefore first saturated in the cold to precipitate as much  $\text{As}_2\text{S}_5$  as possible and then heated to boiling while saturating with  $\text{H}_2\text{S}$  to decompose any oxy-thio acids which may have been formed and thus complete the precipitation of arsenic.

3. At this point the hydrogen ion concentration is approximately 0.3 M. Calculation will show that the sulfide ion concentration obtained from  $\text{H}_2\text{S}$  in 0.3 M acid is adequate for the precipitation of quite small quantities of the elements comprising Group II, but not for those of Group III.

4. If the  $\text{H}_2\text{S}$  treatment produces only a milky white precipitate, it is probable that elements of Group II are absent. The precipitate results from the oxidation of  $\text{H}_2\text{S}$  to free sulfur by ions such as  $\text{Fe}^{+++}$ ,  $\text{CrO}_4^-$ , or  $\text{MnO}_4^-$  in Group III. These elements are of course not necessarily present, hence no change of any sort may be observed upon passing  $\text{H}_2\text{S}$  into a solution from which Group II elements are absent.

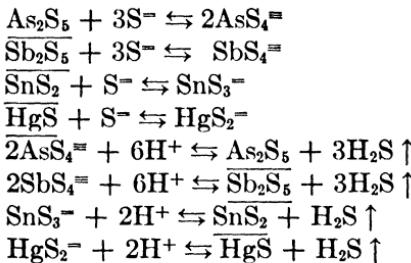
## P 22. Separation of the Copper and Tin Sub-groups.

Treat the precipitate from P 21 with 5 to 10 drops of  $\text{Na}_2\text{S}-\text{NaOH}$  reagent. Stir and warm gently (do not boil). Add 0.5 ml. of  $\text{H}_2\text{O}$  and centrifuge. Reserve the solution, containing elements of the tin subgroup, for P 41. Wash the precipitate with hot water, and treat again with a few drops of  $\text{Na}_2\text{S}-\text{NaOH}$  reagent to insure complete separation. Centrifuge, separate the solution and acidify it with HCl. If the

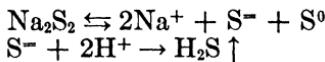
acidification produces a white precipitate, indicating that only sulfur is present, discard. If the precipitate is colored, add the contents of the tube to the solution which is being reserved for treatment by P 41. Treat the residue which was not dissolved by the  $\text{Na}_2\text{S}$ - $\text{NaOH}$  reagent by P 31.

### Notes

1. The separation of arsenic, antimony, tin, and mercury from the copper sub-group depends on the amphoteric properties of these elements (see page 26). The salts which form are analogs of the corresponding oxygen salts, i.e., arsenate and thioarsenate,  $\text{AsO}_4^{=2-}$  and  $\text{AsS}_4^{=2-}$ . Treatment of the solution containing these thio salts with  $\text{HCl}$  reprecipitates the sulfides, since the equilibrium is displaced by removing the sulfide ion as  $\text{H}_2\text{S}$ . The equations for dissolving and reprecipitating the sulfides of Group IIB are given below:



2. If no element of the group is present, acidification of the  $\text{NaOH}$ - $\text{Na}_2\text{S}$  solution produces hydrogen sulfide and free sulfur. This latter is light colored, and not easily mistaken for one of the sulfides, which have more distinct colors ( $\text{As}_2\text{S}_5$  and  $\text{SnS}_2$ , yellow;  $\text{Sb}_2\text{S}_5$ , orange;  $\text{HgS}$ , black). Sulfur results from the decomposition of  $\text{Na}_2\text{S}_2$ , a small amount of which is always present in  $\text{Na}_2\text{S}$ .



3. Other methods of separating Group II into two sub-groups are by the use of: (1) ammonium polysulfide,  $(\text{NH}_4)_2\text{S}_x$ , and (2) by sodium hydroxide. The first reagent, made by dissolving sulfur in  $(\text{NH}_4)_2\text{S}$ , is of unknown composition, but undoubtedly contains some disulfide ion,  $\text{S}_2^{=2-}$ . This ion is an oxidizing agent, and converts arsenic, antimony, and tin to their higher valence states, in which form they are extracted by the sulfide ion present. Thus the need for  $\text{HNO}_3$  oxidation is avoided. Tin must be oxidized to the  $\text{Sn}^{4+}$

state, otherwise its sulfide is not dissolved by sulfide ion. Ammonium polysulfide does not dissolve  $HgS$ , although it dissolves copper sulfide to a certain extent, an undesirable feature. The use of sodium hydroxide in extracting the sulfides of arsenic, antimony and tin is successful if the tin has been previously oxidized, and if  $NH_4Cl$  is present to keep the concentration of hydroxyl ion low. If the hydroxyl ion concentration is too high,  $HgS$  will be partially dissolved. Otherwise, only arsenic, antimony, and tin are separated. Oxy-thio salts are formed from which the sulfides may be reprecipitated upon the addition of  $HCl$ . An advantage claimed for this separation is the absence of large quantities of free sulfur appearing when the thio salts are acidified.

The method used in the present scheme of analysis has the advantage of making a clean separation of mercury from lead, bismuth, copper, and cadmium, thereby simplifying the analysis of these elements. Mercuric sulfide tends to occlude  $CdS$ , hence by dissolving the  $HgS$ , a better separation of these elements is obtained. A small amount of bismuth may be dissolved by this procedure, especially if too much  $Na_2S$ - $NaOH$  reagent has been used. Generally it causes no interference in subsequent procedures, and as the test for bismuth in Group IIA is very sensitive, small losses of the element are not serious.

## GROUP IIA

### P 31. Separation of Lead and Bismuth from Copper and Cadmium.

Transfer the residue from P 22 to a casserole, and dissolve by heating with 0.5 ml. of  $\text{HNO}_3$ . Remove any lumps of free sulfur that may appear. Neutralize the solution with  $\text{NH}_4\text{OH}$ , then add 0.5 ml. in excess, stir thoroughly, and centrifuge the solution, reserving it for P 34. Wash the precipitate with 1 ml.  $\text{H}_2\text{O}$  containing 1 drop of  $\text{NH}_4\text{OH}$ ; discard the washings and treat the precipitate by P 32.

#### Notes

1. Nitric acid is used in dissolving the sulfides because it reduces the concentration of  $\text{S}^{\text{-}}$  in the equilibrium:  $\text{MS} \rightleftharpoons \text{S}^{\text{-}} + \text{M}^{++}$  by oxidizing the  $\text{S}^{\text{-}}$  to free sulfur. The reaction with warm dilute  $\text{HNO}_3$  is:  $3\text{S}^{\text{-}} + 2\text{NO}_3^{\text{-}} + 8\text{H}^{\text{+}} = 3\text{S}^{\text{o}} + 2\text{NO} + 4\text{H}_2\text{O}$ .

2. An excess of ammonium hydroxide is used to precipitate the hydroxides of lead and bismuth, and to convert copper and cadmium into their complex ions,  $\text{Cu}(\text{NH}_3)_4^{++}$  and  $\text{Cd}(\text{NH}_3)_4^{++}$ , which are soluble.

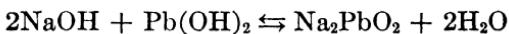
3. Free sulfur may occasionally be dark in color because of the presence of occluded sulfides. It is important that the sulfur be removed before neutralizing with  $\text{NH}_4\text{OH}$ .

### P 32. Detection of Bismuth.

Add 0.5 ml. of  $\text{NaOH}$  to the precipitate from P 31 and boil the solution for about 10 seconds. Add 0.5 ml. of  $\text{H}_2\text{O}$ , filter and wash the precipitate. Reserve the filtrate for P 33; discard the washings. Pour over the precipitate (which should be white) on the filter paper about 1 ml. of freshly prepared sodium stannite solution (see note 2). Black precipitate:  $\text{Bi}^{\text{o}}$ .

#### Notes

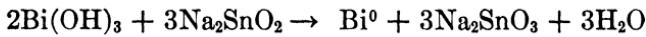
1. The weak amphoteric properties of lead are utilized in separating lead as the soluble plumbite from bismuth, which fails to dissolve in excess  $\text{NaOH}$ .



2. Sodium stannite should be freshly prepared, as it undergoes oxidation upon standing. It is prepared by adding NaOH to a solution of  $\text{SnCl}_2$  until the precipitate which forms just dissolves, then adding several drops in excess.



Bismuth hydroxide, upon treatment with  $\text{Na}_2\text{SnO}_2$ , is reduced to metallic bismuth, which appears as a black precipitate.



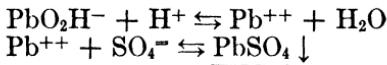
### P 33. Detection of Lead.

Acidify the filtrate from P 32 with  $\text{H}_2\text{SO}_4$ . White precipitate:  $\text{PbSO}_4$ . If a precipitate does not appear immediately, allow the solution to stand 15 minutes before concluding that lead is absent. If a precipitate is obtained, confirm by centrifuging, removing the solution, and treating the residue with a few drops of 3 N  $\text{NH}_4\text{Ac}$  to dissolve it. Warm, if necessary, add 1 drop of HAc and 1 drop of  $\text{K}_2\text{CrO}_4$ . Yellow precipitate:  $\text{PbCrO}_4$ .

### Notes

1. Some lead may escape detection in Group I because of the solubility of  $\text{PbCl}_2$  in water. Hence provision is made for its detection in Group II.

2. Lead sulfate, formed in the reaction



serves as preliminary indication of the presence of lead. Ammonium acetate dissolves lead sulfate forming  $\text{Pb}(\text{Ac})_2$ , a soluble but un-ionized salt. However,  $\text{PbCrO}_4$  is much less soluble than  $\text{PbSO}_4$ , hence, upon the addition of  $\text{K}_2\text{CrO}_4$ ,  $\text{PbCrO}_4$  is precipitated.

### P 34. Detection of Copper.

Acidify one-third of the solution from P 31 with HAc and add 1 drop of  $\text{K}_4\text{Fe}(\text{CN})_6$ . If a red precipitate is obtained, continue to add reagent until precipitation is complete in order to estimate the amount of copper present. Red precipitate:  $\text{Cu}_2\text{Fe}(\text{CN})_6$ .

**Notes**

1. The formation of the pink or red precipitate of  $\text{Cu}_2\text{Fe}(\text{CN})_4$  constitutes a very sensitive test for copper. One part of copper in 1 million parts of solution may be detected by it. Cadmium ferrocyanide also precipitates if cadmium is present at this point, but it is white in color and does not interfere with the copper test.

**P 35. Separation of Copper and Cadmium.**

To one-third of the solution from P 31, add HAc until just acid to litmus. Add 3 drops of salicylaldoxime reagent. Green precipitate: presence of copper. Continue adding salicylaldoxime until precipitation of the copper is complete. Filter, discarding the precipitate. Pass  $\text{H}_2\text{S}$  into the solution. Yellow precipitate:  $\text{CdS}$ .

**Notes**

1. In weakly acid solution, copper is precipitated quantitatively by salicylaldoxime. The test will detect 1 part of copper in 2 million parts of solution. In acid solution cadmium is not precipitated by the reagent, hence a separation of copper and cadmium is possible. Cadmium sulfide may be precipitated from the solution as the acidity is quite low, about 0.01 *M*.

**P 36. Further Confirmation of Cadmium.**

To the remainder of the solution from P 31 add KCN solution, if copper is present, until the solution is decolorized, then add 1 drop in excess. If copper is absent, the KCN may be omitted. Saturate with  $\text{H}_2\text{S}$ . Yellow precipitate:  $\text{CdS}$ .

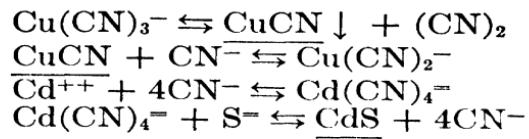
**WARNING:** KCN is poisonous. Use only in alkaline solution; avoid contact with skin.

**Notes**

1. A blue color in the solution from P 31 is due to the complex ion  $\text{Cu}(\text{NH}_3)_4^{++}$ . Potassium cyanide forms with copper ions a complex ion which is dissociated less than the  $\text{Cu}(\text{NH}_3)_4^{++}$ , hence the  $\text{Cu}(\text{NH}_3)_4^{++}$  is transformed into the cyanide complex, and the color is discharged.

There is insufficient  $\text{Cu}^{++}$  in equilibrium with the complex cyanide to permit precipitation of  $\text{CuS}$  in the subsequent step. The cyanide complex of cadmium, however, has an instability constant large enough to allow  $\text{CdS}$  to be precipitated under the same conditions.

The reactions are:



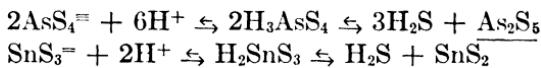
## GROUP IIB

### P 41. Reprecipitation of Group IIB.

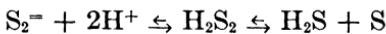
Reprecipitate the sulfides of Group IIB by acidifying the solution from P 22 with HCl until effervescence ceases. Stir well during the acidification. Avoid an excess of acid. If the precipitate is white indicating only sulfur, discard. If the precipitate is at all colored, centrifuge and treat it by P 42. Discard the solution.

#### Notes

1. On acidification of the solution containing the soluble thio-salts of  $Hg^{++}$ ,  $As^{+5}$ ,  $Sb^{+5}$ , and  $Sn^{++++}$ , the corresponding thio-acids are formed. These thio-acids are unstable in acid solution and decompose into the sulfides which are insoluble and  $H_2S$  which escapes. Typical reactions are:



$H_2S_2$ , likewise unstable in acid solution, would be formed if the  $Na_2S$  reagent contained any  $Na_2S_2$ .



Since all the sulfides of this group are colored, a pure white precipitate would be sulfur and show the absence of elements in this group.

### P 42. Separation of Mercury.

Treat the precipitate from P 41 with 5 to 10 drops of 15 N  $NH_4OH$ . Stir thoroughly and warm gently. Add 0.5 ml.  $H_2O$  and pass in  $H_2S$  for 1 minute. A black precipitate indicates mercury. Centrifuge. Treat precipitate by P 43 and solution by P 44.

#### Notes

1.  $HgS$  dissolves readily in  $Na_2S$  or  $NaOH$  solutions but not in  $(NH_4)_2S$  or  $NH_4OH$  solutions because the former give much higher concentrations of  $S^-$  (or  $OH^-$ ) than the latter. The formation of

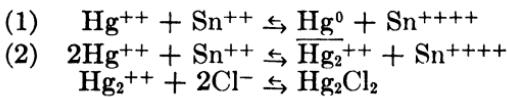
the complex anion,  $\text{HgS}_2^-$ , or the mixed thio-oxy ion,  $\text{HgOS}^-$ , and hence the solubility of  $\text{HgS}$ , is dependent upon the concentration of  $\text{S}^-$ . The other sulfides of this group being more acidic are readily soluble in the more weakly basic  $(\text{NH}_4)_2\text{S}$  or  $\text{NH}_4\text{OH}$ .

### P 43. Confirmation of Mercury.

Dissolve the precipitate from P 42 in a casserole by adding 0.5 ml. of saturated bromine water and 0.5 ml.  $\text{H}_2\text{O}$  and heating. Boil until colorless. Dilute with 1 ml.  $\text{H}_2\text{O}$  and then add  $\text{SnCl}_2$  solution. White or gray precipitate:  $\text{Hg}_2\text{Cl}_2 + \text{Hg}^0$ .

#### Notes

1. Bromine oxidizes  $\text{S}^-$  to free S or even to  $\text{SO}_4^{2-}$  and hence dissolves  $\text{HgS}$ . It is important to remove the excess  $\text{Br}_2$  by boiling before adding  $\text{SnCl}_2$  in order to avoid the oxidation of this reagent by bromine. Two reactions are possible here between  $\text{Hg}^{++}$  and  $\text{Sn}^{++}$ :



### P 44. Precipitation of Arsenic, Antimony, and Tin.

Acidify the solution from P 42 with  $\text{HCl}$  to reprecipitate the sulfides of arsenic, antimony, and tin. Centrifuge. Remove the solution completely and discard it. Add to the precipitate 10 drops of 12 N  $\text{HCl}$ . Heat in a water bath and pass in  $\text{H}_2\text{S}$  for several minutes. A yellow precipitate:  $\text{As}_2\text{S}_5$ . Treat the precipitate by P 45 and the solution by P 46.

#### Notes

1. Use is made here and in P 46 and P 47 of the differences in solubility in acid of the sulfides of arsenic, antimony, and tin.  $\text{As}_2\text{S}_5$  is insoluble in 12 N  $\text{HCl}$  while  $\text{Sb}_2\text{S}_5$  and  $\text{SnS}_2$  are both soluble.  $\text{H}_2\text{S}$  reduces antimony in this procedure from the pentavalent to the trivalent state.  $\text{SbCl}_5 + \text{H}_2\text{S} \rightleftharpoons \text{SbCl}_3 + \text{S}^0 + \text{HCl}$ .  $\text{Sb}_2\text{S}_3$  can be precipitated from a hot solution about 2 N in  $\text{HCl}$  (P 46) while  $\text{SnS}_2$  cannot.  $\text{SnS}_2$  can be precipitated by  $\text{H}_2\text{S}$  in a solution about 1 N in  $\text{HCl}$  (P 48).

2.  $\text{H}_2\text{S}$  is passed into the solution before centrifuging in order to reprecipitate any  $\text{As}_2\text{S}_5$  which may have been dissolved by  $\text{HCl}$  due to loss of  $\text{H}_2\text{S}$  from the hot solution.

**P 45. Detection and Confirmation of Arsenic.**

Add to the precipitate from P 44, 3 drops of 16 *N* HNO<sub>3</sub> and 2 drops of 12 *N* HCl. Heat gently until dissolved and remove any free sulfur that may separate. Neutralize the solution with NH<sub>4</sub>OH and add an equal volume of magnesia reagent. Cool under tap water and stir to start crystallization. Let stand at least 5 minutes. White precipitate: MgNH<sub>4</sub>AsO<sub>4</sub>·6H<sub>2</sub>O. Centrifuge, remove the liquid, and wash the precipitate with NH<sub>4</sub>OH until the washings are nearly free from chloride as shown by adding 1 drop of AgNO<sub>3</sub> and acidifying with HNO<sub>3</sub>. When practically free from chloride add 0.5 ml. H<sub>2</sub>O to the precipitate and then 1 drop of HAc and several drops of AgNO<sub>3</sub>. Red precipitate: Ag<sub>3</sub>AsO<sub>4</sub>.

**Notes**

1. By use of the oxidizing combination HNO<sub>3</sub> and HCl, As<sub>2</sub>S<sub>5</sub> is converted into H<sub>3</sub>AsO<sub>4</sub> and much of the sulfur is oxidized to SO<sub>4</sub><sup>2-</sup>. From a cold alkaline solution magnesia reagent will precipitate MgNH<sub>4</sub>AsO<sub>4</sub>·6H<sub>2</sub>O in fine white crystals. The precipitate forms slowly due to supersaturation and therefore sufficient time should be allowed for crystallization to take place. Stirring hastens the crystallization. The compound is somewhat soluble in water, therefore it is washed with dilute NH<sub>4</sub>OH. The presence of a large amount of Cl<sup>-</sup> would obscure the confirmatory test since AgCl is much less soluble than Ag<sub>3</sub>AsO<sub>4</sub>. HAc dissolves MgNH<sub>4</sub>AsO<sub>4</sub>·6H<sub>2</sub>O.

**P 46. Detection of Antimony.**

Dilute the solution from P 44 containing antimony and tin to exactly 3 ml. Heat to boiling in a water bath and saturate with H<sub>2</sub>S. Orange precipitate: Sb<sub>2</sub>S<sub>3</sub>. Centrifuge, remove the liquid and treat it for tin by P 48. Treat the precipitate by P 47 to confirm antimony.

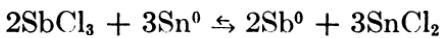
**Notes**

1. The acid concentration given here permits the detection of minimum amounts of antimony even in the hot solution while the same acid concentration and elevated temperature completely prevents the precipitation of tin except that if a large amount of that element is present a small amount of it may come down here. If the precipitate has a brownish appearance, a portion of it should be tested by P 49.

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**P 47. Confirmation of Antimony.**

Add to the precipitate from P 46 5 drops of HCl and boil until dissolved. Add 5 drops of water and a small piece of bright tin. Jet black deposit on the tin: Sb<sup>0</sup>.



Remove the liquid and wash the tin several times with water. Then pour over the tin 0.5 ml. of freshly prepared NaOBr solution (see note 2). If the black deposit remains it confirms the presence of antimony.

**Notes**

1. Tin precipitates antimony from the solution and it appears as a jet black, velvet-like deposit on the tin. Arsenic is also precipitated if present but is distinguished from antimony by its brown-black color and by the fact that it is readily oxidized to arsenate by NaOBr while antimony is not oxidized.

2. Since hypobromite solution rapidly decomposes, with the formation of bromate and bromide, the reagent should be freshly prepared by adding NaOH dropwise to a few drops of saturated Br<sub>2</sub> solution until the solution becomes colorless and then adding one drop in excess.

**P 48. Detection of Tin.**

Add 4 drops of 15 N NH<sub>4</sub>OH to the solution from P 46. Cool and saturate with H<sub>2</sub>S for several minutes. Centrifuge if the solution is not perfectly clear. Yellow precipitate: SnS<sub>2</sub>. Confirm by P 49.

**Notes**

1. The acid solution is partially neutralized with NH<sub>4</sub>OH and cooled in order to decrease the solubility of SnS<sub>2</sub>.

2. The solution is centrifuged here if it is at all cloudy in order to collect the precipitate and insure the detection of small amounts of tin. It is not necessary to separate the precipitate from the solution for the confirmation of tin in P 49.

**P 49. Confirmation of Tin.**

Heat the solution and precipitate obtained in P 48 until the yellow precipitate dissolves, adding a few drops of HCl if necessary. Add a small amount of powdered antimony and heat in a water bath for several minutes. Centrifuge, remove

the solution and add to it first 1 drop and then 0.5 ml. of  $\text{HgCl}_2$ . White or gray precipitate:  $\text{Hg}_2\text{Cl}_2 + \text{Hg}^0$ , which confirms the presence of Sn.

### Notes

1. Heating with HCl dissolves the  $\text{SnS}_2$  and removes the  $\text{H}_2\text{S}$  formed. Antimony reduces  $\text{SnCl}_6^-$  to  $\text{Sn}^{++}$  which permits the confirmation of tin with  $\text{HgCl}_2$ .



A single drop of  $\text{HgCl}_2$  is added first in order to favor the precipitation of black metallic mercury which is more distinctive than the white  $\text{Hg}_2\text{Cl}_2$  which is formed in the presence of an excess  $\text{HgCl}_2$ . More  $\text{HgCl}_2$  is added later in order that the size of the precipitate may be used to estimate the amount of tin present.

### P 50. Detection and Removal of Phosphate.

Treat 1 to 2 drops of the solution from P 21 with 1 drop of  $\text{HNO}_3$  and boil to remove  $\text{H}_2\text{S}$ . Add 5 drops of  $(\text{NH}_4)_2\text{MoO}_4$  solution and heat to 60–70°. Bright yellow precipitate:  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ , or  $(\text{NH}_4)_3(\text{P}[\text{Mo}_3\text{O}_{10}]_4)$ .

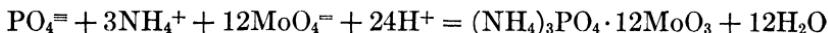
If phosphate is absent, treat the remainder of the solution from P 21 by P 51. If phosphate is present, evaporate the solution until only a few drops remain. Add 5 to 6 drops of 16 N  $\text{HNO}_3$  and evaporate nearly to dryness. Again add 2 to 3 drops of 16 N  $\text{HNO}_3$  and repeat the evaporation. Add a few drops of  $\text{H}_2\text{O}_2$ , transfer to a 10 ml. test tube and dilute to about 2 ml. Neutralize the solution to litmus with  $\text{NH}_4\text{OH}$ ; then acidify carefully with  $\text{HNO}_3$ . Add 4 drops in excess and dilute to exactly 3 ml. Place the tube in a boiling water bath and when hot add 0.1 M  $\text{Bi}(\text{NO}_3)_3$  solution, 5 drops at a time, until the precipitation of  $\text{BiPO}_4$  is complete. Then add a few drops in excess. Digest for several minutes to coagulate the precipitate, and centrifuge. Test the solution with another drop of  $\text{Bi}(\text{NO}_3)_3$ . When the phosphate has been completely precipitated, pipette off the solution and treat it according to the next paragraph. Discard the precipitate of  $\text{BiPO}_4$ .

Saturate the solution obtained above with  $\text{H}_2\text{S}$  to precipitate the bismuth as  $\text{Bi}_2\text{S}_3$ . Centrifuge, remove the solution,

add 1 to 2 drops of  $\text{NH}_4\text{OH}$  but do not neutralize, and pass in  $\text{H}_2\text{S}$ . If more  $\text{Bi}_2\text{S}_3$  is formed, centrifuge and remove the solution. Boil the solution and evaporate, if necessary, to about 2 ml. and treat by P 51.

#### Notes

1.  $(\text{NH}_4)_2\text{MoO}_4$  precipitates  $\text{PO}_4^{=}$  in a warm nitric acid solution as the voluminous, bright yellow ammonium phosphomolybdate.



2. If phosphate were present, it would interfere with the separation and identification of the ions of Groups III and IV since it would cause precipitation of these ions whenever the solution was made alkaline. Most phosphates, however (except  $\text{BiPO}_4$ ), are readily soluble in 0.3 *N* acid and hence no interference is experienced in the precipitation of the earlier groups. In the case of bismuth, although its phosphate is insoluble in 0.3 *N* acid,  $\text{Bi}_2\text{S}_3$  is so much less soluble than  $\text{BiPO}_4$  that the latter is completely transformed into  $\text{Bi}_2\text{S}_3$  by  $\text{H}_2\text{S}$  passed into a suspension of the phosphate in dilute acid.

3. P 50 provides for the detection of phosphate in the filtrate from the  $\text{H}_2\text{S}$  precipitation and its removal before the precipitation of the iron-aluminum group is begun. The removal of phosphate depends upon the fact that  $\text{Bi}^{+++}$  alone among the metallic ions considered in this scheme forms a phosphate insoluble in 0.5 *N*  $\text{HNO}_3$ . Chloride ion, however, must be absent because  $\text{BiPO}_4$  is much more soluble in  $\text{HCl}$  than in  $\text{HNO}_3$  due to the formation of soluble  $\text{HBiCl}_4$ , and because the formation of the slightly soluble  $\text{BiOCl}$  would use up much of the reagent needed for the phosphate.  $\text{HCl}$  is therefore removed by repeated evaporation with  $\text{HNO}_3$ . After dilution and neutralization the acidity is adjusted to 0.5 *N* with  $\text{HNO}_3$  and an excess of  $\text{Bi}(\text{NO}_3)_3$  is added to precipitate  $\text{PO}_4^{=}$ . After removal of the  $\text{BiPO}_4$  precipitate, the excess  $\text{Bi}^{+++}$  is removed with  $\text{H}_2\text{S}$ . In order to be certain that bismuth, which would interfere in later procedures, has been completely removed, it is recommended that the acidity be reduced and the solution again saturated with  $\text{H}_2\text{S}$ .

**PRECAUTION.** Do not neutralize the solution completely at this point since sulfides of the iron-aluminum group would be precipitated and lost. According to Swift,\* less than 1 mg. of Fe, Al, Co, Ni, Zn is carried down with the  $\text{BiPO}_4$  precipitate when 500 mg.  $\text{PO}_4^{=}$  are present with 250 mg. of any one of these elements. Under the same conditions 12 to 15 mg. of Cr may be precipitated giving a greenish tinge to the white  $\text{BiPO}_4$  precipitate.

\* "A System of Chemical Analysis," pages 305-306, Prentice-Hall, Inc., New York, 1939.

## GROUP III

### P 51. Precipitation of Zinc.

Boil the solution from P 21 or P 50, if phosphate has been found present, until the odor of  $H_2S$  can no longer be detected. Neutralize the solution with  $NH_4OH$  to litmus, then add 1 drop of HCl. The volume of solution at this point should not exceed 2.5 ml. Add 5 drops of formate buffer (and 1 drop of acrolein if desired). Pass  $H_2S$  into the solution until a precipitate appears, then for an additional 10 or 15 seconds. White or gray precipitate:  $ZnS$ . Centrifuge the precipitate, wash twice with 0.5 ml. portions of hot water. Reserve the solution for P 61.

In the presence of large quantities of iron, cobalt, or nickel, the precipitate may initially be grayish-white, then turn black. If this occurs, the precipitate should be centrifuged (reserving the solution for P 61), and washed with 0.5 ml. of hot water. Dissolve the precipitate in the minimum amount of HCl, dilute to about 2 ml., and treat as in the above paragraph to reprecipitate  $ZnS$ . Add the solution to that being reserved for P 61.

In either case, confirm zinc by P 52.

### Notes

1. Boiling the solution to remove  $H_2S$  avoids formation of sulfides of Group III during the neutralization. The presence of these sulfides would be undesirable because of their color, and because of the difficulty in redissolving them.

2. Zinc is precipitated quantitatively by  $H_2S$  from solutions of pH 2 to 3, a value which is obtained by use of the formic acid-ammonium formate buffer. At this pH the sulfide ion concentration in equilibrium with  $H_2S$  is still too small to precipitate sulfides of Group III elements such as Mn, Fe, Co, Ni.

3. Many freshly precipitated sulfides are colloidal, which makes them difficult to filter or centrifuge. Among these are  $ZnS$ ,  $SnS_2$ ,  $CoS$ ,  $NiS$ . Likewise, in the case of  $ZnS$ , the freshly precipitated sulfide carries down elements such as cobalt and nickel (probably

others) from Group III. As the zinc sulfide is peptized by a layer of sulfide or hydrosulfide ions, the entrainment of foreign elements probably involves a reaction with these peptizing ions. Various unsaturated aldehydes, of which acrolein and crotonaldehyde are examples, react with the peptizing layer and remove it. Thus the precipitate is flocculated, rendering it easily filtered or centrifuged, and danger of entrainment is diminished.

4. A milky suspension may appear in P 51 which should not be mistaken for zinc sulfide. The white material consists either of sulfur, formed in the oxidation of  $H_2S$  by Group III elements, or of resinous products formed from the acrolein. The material may be difficult to centrifuge, but in any case should be treated by P 52 to confirm zinc.

#### P 52. Confirmation of Zinc.

Dissolve the precipitate of zinc sulfide, P 51, in a few drops of 2*N*  $HNO_3$  and boil to remove  $H_2S$ . With a capillary pipette transfer a drop or two of the solution to a small strip of potassium cobalticyanide paper. Dry by holding the paper in forceps high above a small flame. Continue drying until the spot turns brown. Then light the paper and place the ash on a spot plate. A disk of green ash where the drop of solution was added confirms zinc.

#### Notes

1. The above test is known as Rinman's Green test for zinc and has been modified by Benedetti-Pichler for the microtechnic.\* Certain elements interfere: tin and antimony (because they form a green ash), manganese, iron, cobalt, and nickel (because they give precipitates with potassium cobalticyanide and dark residues on ashing).

2. In case the zinc sulfide precipitate is dark colored, it may be washed and then dissolved in a little dilute  $HNO_3$  and treated with  $NaOH$  and  $Na_2O_2$  to remove manganese, nickel, cobalt, and iron. Filter; from the filtrate the zinc is again precipitated with  $H_2S$ . The  $ZnS$  is finally dissolved in 2*N*  $HNO_3$  and this solution used for the Rinman's Green test. The residue of manganese, nickel, etc., is dissolved in a few drops of  $HCl$  and added to the solution obtained in P 62.

#### P 61. Precipitation of Iron and Aluminum Sub-groups.

Boil the solution from P 51 to remove  $H_2S$ , then neutralize with  $NH_4OH$ . A white precipitate indicates  $Al^{+++}$  or  $Fe^{++}$ ;

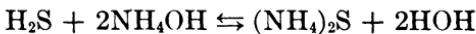
\* A. A. Benedetti-Pichler, Ind. Eng. Chem., Anal. Ed. 4, 336 (1932).

a colored precipitate may be due to  $\text{Co}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Fe}^{+++}$ , or  $\text{Cr}^{+++}$ . Add 0.5 ml. of  $\text{NH}_4\text{Cl}$  solution, stir thoroughly and pass in  $\text{H}_2\text{S}$  for 2 minutes. Centrifuge any precipitate and reserve for treatment by P 62. Treat the solution by P 91.

### Notes

1. Removal of  $\text{H}_2\text{S}$ , followed by the addition of  $\text{NH}_4\text{OH}$ , allows observation of the hydroxides that may form, thus affording preliminary information regarding the elements to be expected in later separations. During the subsequent treatment with  $\text{H}_2\text{S}$ , aluminum and chromium remain as the hydroxides.

The hydroxides of the remaining elements are converted into sulfides by the  $\text{H}_2\text{S}$ , since the sulfides are less soluble than the hydroxides. Furthermore, the concentration of sulfide ion is greatly increased in alkaline solution as a result of the reaction:



in which the product  $(\text{NH}_4)_2\text{S}$  is highly ionized.

2. Addition of the  $\text{NH}_4\text{Cl}$  supplies ammonium ion to repress the ionization of  $\text{NH}_4\text{OH}$  (by the common ion effect), thus lowering the  $(\text{OH}^-)$ . This is necessary to prevent precipitation of magnesium hydroxide in Group III, which might occur if the  $(\text{OH}^-)$  were too high.

3. The colors of the hydroxides are as follows:  $\text{Al}(\text{OH})_3$ , white;  $\text{Fe}(\text{OH})_2$ , white, rapidly changing to green or brown;  $\text{Fe}(\text{OH})_3$ , reddish-brown;  $\text{Cr}(\text{OH})_3$ , gray-green;  $\text{Mn}(\text{OH})_2$ , white, turning to dark brown upon air oxidation. Nickel and cobalt hydroxides may precipitate momentarily but redissolve in the  $\text{NH}_4\text{OH}$  upon formation of the complex ions.

### P 62. Separation of Iron and Aluminum Sub-groups.

Wash the precipitate from P 61 twice with 0.5 ml. portions of  $\text{NH}_4\text{OH}$ , discarding the washings. Dissolve the precipitate in the minimum amount of  $\text{HCl}$ , adding a few drops of bromine if necessary, heating to assist in dissolving. Transfer the solution to a casserole, add excess  $\text{NaOH}$ , followed by as much solid  $\text{Na}_2\text{O}_2$  as can be contained in the rounded bottom of a 5 ml. test tube. Stir well, filter the solution on hardened filter paper, collecting the filtrate in a clean test tube. Reserve the solution for treatment by P 71. Wash the precipitate with 5 to 10 drops of hot water, discarding the

washings. If there is no visible material on the filter paper after washing, the absence of iron, cobalt, nickel, and manganese may be concluded. However, even a slight dark stain on the paper should not be disregarded, but should be tested by P 81. If the filtrate from the  $\text{NaOH}-\text{Na}_2\text{O}_2$  treatment has a yellow color, chromium (as  $\text{CrO}_4^{2-}$ ) is indicated.

#### Notes

1. When freshly precipitated,  $\text{CoS}$  and  $\text{NiS}$  are soluble in dilute acid. Upon standing, they are believed to undergo a change in crystal structure and become very difficult to dissolve in acid. Bromine assists in dissolving them.
2. Treatment with excess  $\text{NaOH}-\text{Na}_2\text{O}_2$  dissolves the amphoteric hydroxides of aluminum and beryllium (if included in the analysis), converts  $\text{Mn}(\text{OH})_2$  into hydrated manganese dioxide,  $\text{MnO}_2 \cdot \text{H}_2\text{O}$  (or  $\text{MnO}(\text{OH})_2$ ); oxidizes the chromium to chromate; oxidizes the cobalt to  $\text{Co}(\text{OH})_3$ ; does not affect the nickel. Cobaltic hydroxide is later reduced by water to cobaltous hydroxide, which is more stable.
3. Hardened filter paper, which is alkali resistant, should be used for the filtration. Ordinary filter paper disintegrates rapidly under the influence of strong alkali.

## GROUP IIIA

### P 71. Separation of Aluminum and Chromium.

Acidify the alkaline solution from P 62 with HCl, then make weakly basic by dropwise addition of  $\text{NH}_4\text{OH}$ . White precipitate:  $\text{Al}(\text{OH})_3$ . Heat to coagulate the precipitate; filter, reserving the filtrate for P 73. Treat the precipitate by P 72.

#### Notes

1. Addition of HCl causes the equilibrium



to be shifted to the right by removing the  $\text{OH}^-$  ions as water. Upon adding the acid, a precipitate first appears  $[\text{Al}(\text{OH})_3]$  which later dissolves as the  $\text{H}^+$  is increased.

In reprecipitating the hydroxide, a weak base such as ammonia is used to keep the  $[\text{OH}^-]$  low enough to prevent redissolving of the amphoteric  $\text{Al}(\text{OH})_3$ .

### P 72. Confirmation of Aluminum.

Dissolve the precipitate from the filter paper with a few drops of warm HCl. To the solution obtained add 3 drops of  $\text{NH}_4\text{Ac}$  solution and 3 drops of aluminon reagent. Make the solution alkaline by the addition of  $(\text{NH}_4)_2\text{CO}_3$ , adding 2 or 3 drops in excess. Boil. A red precipitate indicates the presence of aluminum.

#### Notes

1. "Aluminon" (ammonium aurin tricarboxylate) is a dye capable of forming brilliantly colored lakes with several metals. The aluminum lake, which is bright red in color, forms in an acetate buffer mixture. The solution is then made alkaline with ammonia and ammonium carbonate for two reasons: (1) Chromium forms a lake resembling that of aluminum, but this is destroyed in ammoniacal solution. (2) Alkaline earth metals also form colored lakes, but these are decomposed by the ammonium carbonate.

Iron, if present, forms a violet-colored lake, converted to reddish brown  $\text{Fe}(\text{OH})_3$  upon the addition of ammonia; if there is doubt

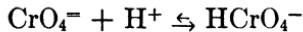
as to the exact color of the aluminum salt, a solution known to contain aluminum should be tested.

**P 73. Detection of Chromium.**

Acidify the filtrate from P 71 with acetic acid, add 3 drops of lead acetate and heat to boiling. Yellow precipitate:  $\text{PbCrO}_4$ .

**Notes**

1. Lead chromate is less soluble in a solution of a weak acid than in HCl, since in strong acid the reaction:



is effective in removing  $\text{CrO}_4^-$  ions from the equilibrium  $\text{PbCrO}_4 \rightleftharpoons \text{Pb}^{++} + \text{CrO}_4^-$ , in turn causing  $\text{PbCrO}_4$  to dissolve.

## GROUP III B

### P 81. Separation of Manganese.

Pour into the filter paper, containing the precipitate from P 62, 2 ml. of hot  $\text{HNO}_3$  to which 1 drop of  $\text{NaClO}_3$  solution has been added. Collect the solution in a clean test tube and reserve for treatment by P 83. A brown or black residue on the filter paper may be  $\text{MnO}_2$ . P 82 should be carried out to confirm manganese.

#### Notes

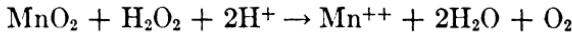
1. Iron, cobalt, and nickel hydroxides, which may be on the filter paper at this point, dissolve readily in the mixture of nitric and chloric acids. The oxidizing action of the acids prevents any reduction of the brown or black  $\text{MnO}_2$ , hence this appears as a residue if manganese is present. For small amounts of manganese (0.1 mg.), the residue may be no more than a stain on the paper; it should, however, be confirmed by P 82.

### P 82. Confirmation of Manganese.

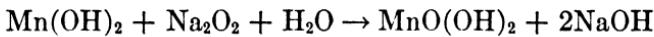
Pour over the precipitate on the filter paper 1 ml. of warm  $\text{HNO}_3$  containing 5 drops of  $\text{H}_2\text{O}_2$ . Collect the solution and place several drops of it on a spot plate. Add a small amount of  $\text{NaBiO}_3$ . Purple color:  $\text{HMnO}_4$ .

#### Notes

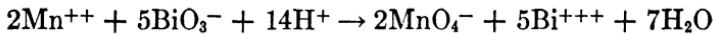
1. The reaction between  $\text{H}_2\text{O}_2$  and  $\text{MnO}_2$  in acid solution is as follows:



Under these conditions, hydrogen peroxide is a reducing agent, as it is when reacting with permanganate. Hydrogen peroxide in acid solution is a reducing agent. When used in alkaline solution (where it exists as sodium or potassium peroxide), its action is that of an oxidizing agent. Use is made of this property in P 62 (see note 2).



2. Sodium bismuthate is a powerful oxidizing agent, converting manganous salts directly into permanganate.



**P 83. Detection of Iron.**

Pour the filtrate from P 81 into 1 ml. of concentrated  $\text{NH}_4\text{OH}$ . Stir well. Test with litmus to assure that the solution is strongly basic; if not, add another ml. of  $\text{NH}_4\text{OH}$ . Red-brown precipitate:  $\text{Fe}(\text{OH})_3$ . Confirm by centrifuging the precipitate and treating by P 84. Solution: P 85 and P 86.

**Notes**

1. In concentrated  $\text{NH}_4\text{OH}$ , cobalt and nickel hydroxides precipitate, then redissolve upon formation of the complex ions  $\text{Co}(\text{NH}_3)_6^{4+*}$  and  $\text{Ni}(\text{NH}_3)_6^{2+}$ , while iron precipitates as the hydroxide, which fails to redissolve. Small amounts of cobalt and nickel are carried down by the iron, but this loss is not serious and these elements do not interfere in the subsequent test for iron.

**P 84. Confirmation of Iron.**

Dissolve the precipitate from P 83 in HCl. To 1 or 2 drops of the solution add 1 drop of  $\text{NH}_4\text{CNS}$  solution. Red color: ferric thiocyanate complex.

**Notes**

1. Dissolving the  $\text{Fe}(\text{OH})_3$  in HCl gives a solution of  $\text{Fe}^{3+}$ , easily identified by the red thiocyanate complex. The exact nature of the colored compound appears to be unsettled, although evidence indicates the existence of  $\text{Fe}(\text{CNS})_2^+$ ,  $\text{Fe}(\text{CNS})_6^{4-}$ , or  $\text{Fe}(\text{CNS})_4^-$ , as possible sources of the color.

**P 85. Detection of Nickel.**

To 3 drops of the solution from P 83, add on a spot plate 1 or 2 drops of dimethylglyoxime. Bright red precipitate: presence of nickel.

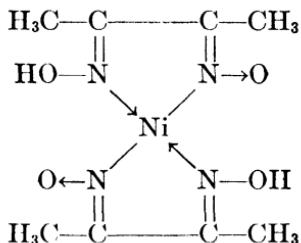
**Notes**

1. Other ions giving red precipitates with dimethylglyoxime are  $\text{Fe}^{3+}$  and  $\text{Pd}^{2+}$ . The test for nickel is extremely sensitive; 1 part of  $\text{Ni}^{2+}$  in 3 million parts of solution may be detected. Formation of the red salt depends on the presence of the group



\* Probably this ion rather than  $\text{Co}(\text{NH}_3)_6^{4+}$ , since the latter compound is a powerful reducing agent, unstable in water.

in the organic reagent. The nickel salt of dimethylglyoxime is formed from two molecules of reagent and one nickel ion:



### P 86. Detection of Cobalt.

Acidify 0.5 ml. of the solution from P 83 in a test tube with sulfuric acid. Add solid  $\text{NH}_4\text{CNS}$  until the solution is nearly saturated. Add 1 ml. of amyl alcohol and shake well. A blue color in the alcohol layer: cobalt thiocyanate complex.

As an alternative test for cobalt, acidify 3 drops of the solution from P 83 on a spot plate with HAc, and to a drop of this solution on a filter paper add 1 drop of freshly prepared alpha nitroso beta naphthol reagent. A reddish-brown spot indicates the presence of cobalt. For comparison, the test should be performed on a solution containing cobalt.

## Notes

1. Cobalt forms a complex ion in water with  $\text{CNS}^-$ , either  $\text{Co}(\text{CNS})_2$  or  $(\text{NH}_4)_2\text{Co}(\text{CNS})_4$ , which is soluble in amyl alcohol. When a solution containing the complex is shaken with amyl alcohol, the complex is concentrated in the alcohol layer, and imparts a blue color to it. Nickel does not interfere in the reaction unless there are large quantities of it present. Then the color of the  $\text{Ni}^{++}$  obscures the color of the complex. Ferric iron interferes with the test, since it forms a red complex with thiocyanate (see above). Fluoride ion may be added to mask the color of the iron, since it removes  $\text{Fe}^{+++}$  from solution in the form of the complex  $\text{FeF}_6^-$ .

The alternative test for cobalt with alpha nitroso beta naphthol is likewise specific for cobalt in the presence of nickel, and is about ten times more sensitive than the amyl alcohol test. As the reagent itself is colored, it is advisable to test a known solution for comparison.

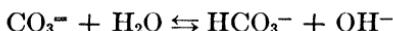
## GROUP IV

### P 91. Removal of Ammonium Salts.

Acidify the filtrate from P 61 with HCl, boil to remove H<sub>2</sub>S, centrifuge and pipette the liquid from any residue. Transfer the liquid to a small casserole, evaporate to dryness, and ignite (heat strongly) until ammonium salts have been volatilized. Do not heat the casserole to redness. Allow the casserole to cool, moisten the residue with 1 to 2 drops 12 N HCl. Dilute with 1 ml. H<sub>2</sub>O, warm, if necessary, to dissolve and transfer to a 10 cm. test tube. Treat by P 92.

### Notes

1. The filtrate from P 61 will contain considerable amounts of ammonium salts. Some may have been present in the original solution, others have been formed in the course of the early procedures by neutralization of various acids with NH<sub>4</sub>OH. While a moderate concentration of NH<sub>4</sub><sup>+</sup> is necessary to prevent the precipitation of magnesium, too high a concentration may so reduce the concentration of CO<sub>3</sub><sup>2-</sup> in the subsequent precipitation that the other carbonates of this group may be only incompletely precipitated. This may be deduced from the following considerations. (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> is a salt of a weak base and a very weak acid and, therefore, is largely hydrolyzed.



The addition of NH<sub>4</sub><sup>+</sup> lowers the concentration of OH<sup>-</sup> by the reaction: NH<sub>4</sub><sup>+</sup> + OH<sup>-</sup> ⇌ NH<sub>3</sub> + H<sub>2</sub>O and thus reduces the concentration of CO<sub>3</sub><sup>2-</sup> still further. The accumulated ammonium salts are therefore removed by volatilization and their concentration, as well as that of NH<sub>4</sub>OH, is later (P 92) adjusted to insure the precipitation of BaCO<sub>3</sub>, SrCO<sub>3</sub>, CaCO<sub>3</sub>, but not MgCO<sub>3</sub>. This is possible since the solubility product MgCO<sub>3</sub> is larger than the solubility products of the other three carbonates.

2. Heating to redness is avoided to prevent volatilization of NaCl and KCl. Magnesium salts hydrolyze during ignition forming basic salts insoluble in water. HCl converts them into soluble compounds.

**P 92. Precipitation of Alkaline Earth Group.**

Add 6 drops 3 *N* NH<sub>4</sub>Cl to the solution prepared in P 91, neutralize with 15 *N* NH<sub>4</sub>OH and add 1 drop in excess. Heat nearly to boiling in a water bath and add 3 to 5 drops 3 *M* (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> reagent. Continue heating in water bath for several minutes and test for completeness of precipitation with another drop of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>. Centrifuge and wash the precipitate twice with distilled water. Precipitate, P 93. Solution, P 101.

**Notes**

1. This separation of magnesium from the other alkaline earth elements is satisfactory except that if a large amount of magnesium is present MgCO<sub>3</sub> may be partially precipitated also. Provision is therefore made for the detection of magnesium in Group IV as well as in Group V because its presence in one or both groups gives an indication of the amount present.

**P 93. Separation of Calcium (and Magnesium) from Barium and Strontium.**

Dissolve the precipitate from P 92 in a few drops of HNO<sub>3</sub>. Transfer to a small beaker and evaporate just to dryness on a hot plate or on an asbestos pad over a free flame. Add 1 ml. methyl alcohol. Stir thoroughly, breaking up lumps of precipitate with the stirring rod. Allow to settle and decant the liquid into a 3 cm. test tube leaving as much of the precipitate as possible in the beaker. Extract with a second 1 ml. portion methyl alcohol and decant the liquid into the same tube. If the liquid is at all cloudy, centrifuge, pipette off the liquid, transfer it to a small beaker and treat it by P 94. Treat the residue insoluble in methyl alcohol by P 96.

**Notes**

1. Most salts are insoluble in organic solvents, even in the somewhat polar solvents such as alcohols and acetone. This insolubility is due to the large electrostatic forces of the ionic lattices of most salts. That these forces are weaker in Ca(NO<sub>3</sub>)<sub>2</sub> is evidenced by the large solubility of this salt in water as compared with Mg(NO<sub>3</sub>)<sub>2</sub>, Sr(NO<sub>3</sub>)<sub>2</sub>, and Ba(NO<sub>3</sub>)<sub>2</sub>. The solubilities of these salts in water

and in methyl alcohol are shown in the following table:

SALT	SOLUBILITY IN H <sub>2</sub> O g. per 100 g. sat. soln. at 25° C.	SOLUBILITY IN CH <sub>3</sub> OH g. per 100 g. CH <sub>3</sub> OH at 25° C.
Mg(NO <sub>3</sub> ) <sub>2</sub>	42.1	17.3 20° C.
Ca(NO <sub>3</sub> ) <sub>2</sub>	57.98	65.5
Sr(NO <sub>3</sub> ) <sub>2</sub>	40.7 20° C.	0.08
Ba(NO <sub>3</sub> ) <sub>2</sub>	9.27	0.057 20° C.

Advantage is taken of these differences in solubility in methyl alcohol to separate calcium (and magnesium) from strontium and barium.

#### P 94. Detection of Calcium.

Evaporate the CH<sub>3</sub>OH solution from P 93 just to dryness. Dissolve in 1 ml. H<sub>2</sub>O, heat in a water bath and add 2 drops (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. If a white precipitate forms indicating calcium, continue the addition of (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> dropwise until precipitation is complete. Heat in the water bath until the precipitate is coarsely granular and has settled. Centrifuge. White precipitate: CaC<sub>2</sub>O<sub>4</sub>. Treat solution by P 95.

#### P 95. Detection of Magnesium.

To the solution from P 94, add 5 drops Na<sub>2</sub>HPO<sub>4</sub> and 5 drops NH<sub>4</sub>OH. Cool thoroughly, stir and let stand for at least 5 to 10 minutes. White crystalline precipitate: MgNH<sub>4</sub>PO<sub>4</sub>·6H<sub>2</sub>O.

#### Notes

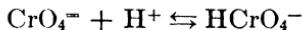
1. MgNH<sub>4</sub>PO<sub>4</sub>·6H<sub>2</sub>O is appreciably soluble even in cold water; therefore the volume should be kept small and an excess of NH<sub>4</sub>OH should be used. The precipitate, which may form slowly, is distinctly crystalline.

#### P 96. Detection of Barium.

Dissolve the residue from P 93 in 1 to 2 ml. of water. Add 1 drop HAc and 5 drops NH<sub>4</sub>Ac. Heat nearly to boiling in a water bath and add 1 to 3 drops K<sub>2</sub>CrO<sub>4</sub>. Allow the precipitate to settle or centrifuge and test for completeness of precipitation by adding 1 to 2 drops more K<sub>2</sub>CrO<sub>4</sub>. When precipitation is complete, centrifuge and remove the liquid. Yellow precipitate: BaCrO<sub>4</sub>. Treat the solution by P 97.

**Notes**

1. The concentration of  $\text{CrO}_4^{=}$  is adjusted by regulating the pH of the solution so that  $[\text{Ba}^{++}][\text{CrO}_4^{=}] > S_{\text{BaCrO}_4}$  while  $[\text{Sr}^{++}][\text{CrO}_4^{=}] < S_{\text{SrCrO}_4}$ . This is possible since  $\text{HCrO}_4^{-}$  is a weak acid and the addition of  $\text{H}^{+}$  must result in a decrease in  $[\text{CrO}_4^{=}]$ .



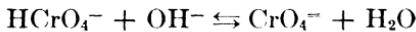
2. It is very important that barium be completely precipitated before the solution is tested for strontium, otherwise  $\text{BaSO}_4$  would precipitate along with  $\text{SrSO}_4$ . Therefore the test for completeness of precipitation should not be omitted.

**P 97. Detection of Strontium.**

Neutralize the solution from P 96 with  $\text{NH}_4\text{OH}$  and add 2 drops in excess. Heat in a water bath at 60–70° C. and add dropwise, with stirring, one-half volume of  $\text{C}_2\text{H}_5\text{OH}$ . Heat for several minutes, cool under tap water and centrifuge. Yellow precipitate:  $\text{SrCrO}_4$ . Wash the precipitate once with a few drops of cold  $\text{H}_2\text{O}$  and then add to the precipitate 1 drop  $\text{NH}_4\text{OH}$ , 1 drop  $\text{K}_2\text{CrO}_4$ , and 15 drops  $\text{H}_2\text{O}$ . Heat to boiling and then centrifuge. Pipette out the liquid and add to it 1 to 3 drops  $(\text{NH}_4)_2\text{SO}_4$ . Heat and let stand for several minutes. Fine white precipitate:  $\text{SrSO}_4$ .

**Notes**

1. Neutralization of the acid results in a large increase in the concentration of the  $\text{CrO}_4^{=}$ .



and makes the ion product  $[\text{Sr}^{++}][\text{CrO}_4^{=}]$  greater than the solubility product for  $\text{SrCrO}_4$ . The addition of alcohol further decreases the solubility of this compound. The alcohol should be added slowly with thorough stirring and the precipitate digested in order to make it more coarsely granular. Too large a proportion of  $\text{C}_2\text{H}_5\text{OH}$  will cause precipitation of potassium and ammonium salts.

## GROUP V

### P 101. Removal of Ammonium Salts.

Evaporate the solution from P 92 to dryness in a casserole, and carefully ignite until white fumes cease to be evolved. Do not heat to redness. Cool, moisten the residue with 3 to 4 drops of concentrated HCl; repeat the evaporation and ignition. Cool, add 4 to 10 drops of water, depending on the amount of residue. Treat portions of the solution by P 102, P 103, P 104, P 105.

#### Notes

1. The ignition of the sample serves to decompose ammonium salts introduced in P 92. Salts such as  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_3$ , etc., volatilize as such or may decompose into simpler substances such as HCl,  $\text{NH}_3$ ,  $\text{N}_2\text{O}$ . Heating the sample to redness should be avoided, since some NaCl or KCl might be lost through volatilization.

### P 102. Precipitation of Magnesium.

To 3 drops of the solution from P 101 in a small test tube, add 2 drops  $\text{Na}_2\text{HPO}_4$  and 2 drops  $\text{NH}_4\text{OH}$ . Cool thoroughly, stir and let stand. White crystalline precipitate:  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ . Confirm by P 103.

#### Notes

1. See note P 95.

### P 103. Confirmation of Magnesium.

Centrifuge the precipitate obtained in P 102, discarding the solution. Dissolve in a few drops of HCl, and dilute to 0.5 ml. Add 2 drops of "magneson" reagent, then NaOH to make the solution distinctly alkaline. A blue precipitate confirms magnesium.

#### Notes

1. "Magneson" is a complex organic compound, para nitrobenzene azoresorcinol. Under conditions of the test, magnesium

is the only element which will precipitate with it. If in doubt as to the appearance of the magnesium derivative, a known solution should be tested.

#### P 104. Detection of Potassium.

To 1 drop of the solution from P 101, in a constricted centrifuge tube, add 2 drops of freshly prepared sodium cobaltinitrite, shake well and centrifuge. Yellow precipitate:  $\text{KNa}_2\text{Co}(\text{NO}_2)_6$  or  $\text{K}_2\text{NaCo}(\text{NO}_2)_6$ . Additional evidence for potassium may be obtained from P 105.

#### Notes

1. Potassium reacts with  $\text{Na}_3\text{Co}(\text{NO}_2)_6$  to form the insoluble salts  $\text{KNa}_2\text{Co}(\text{NO}_2)_6$  and  $\text{K}_2\text{NaCo}(\text{NO}_2)_6$ . Ammonium ion likewise forms a yellow precipitate with the reagent,  $\text{NH}_4\text{Na}_2\text{Co}(\text{NO}_2)_6$  and  $(\text{NH}_4)_2\text{NaCo}(\text{NO}_2)_6$ . The test is very sensitive, and under proper conditions the potassium is quantitatively precipitated. Only the freshly prepared reagent should be used, since it decomposes fairly readily upon standing. If doubt exists as to the freshness of the reagent, a known solution of potassium should be tested.

#### P 105. Detection of Sodium.

To 1 drop of the solution from P 101, in a constricted centrifuge tube, add 2 drops of zinc uranyl acetate solution, shake well, and centrifuge. Yellow precipitate:  $\text{Na}(\text{UO}_2)_3 \cdot \text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_9 \cdot 6\text{H}_2\text{O}$ . In the presence of much potassium, a precipitate of a double salt, potassium uranyl acetate  $\text{KUO}_2(\text{C}_2\text{H}_3\text{O}_2)_3$ , may be formed.\* The fine, needle-like crystals of the potassium salt are not easily mistaken for the sodium salt, however. Additional evidence for sodium may be obtained from P 105.

#### Notes

1. Uranyl acetate,  $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$ , in the presence of the acetates of  $\text{Zn}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Fe}^{++}$ , forms with sodium an insoluble salt having the composition  $\text{Na}(\text{UO}_2)_3\text{M}(\text{C}_2\text{H}_3\text{O}_2)_9 \cdot 6\text{H}_2\text{O}$ . Precipitation of the salt is frequently slow, several minutes being required before the coarse crystals appear. By this test, as little as 0.01 mg. of sodium may be detected. The test is inconclusive when there is 100 times as much potassium as sodium present.

\* Caley and Baker, Ind. Eng. Chem., Anal. Ed. 11, 604 (1939).

### P 106. Flame Tests for Potassium and Sodium.

Introduce a drop of the solution from P 101 into a flame by means of a nichrome wire loop. A violet flame, when viewed through cobalt glass, indicates potassium. A yellow flame, viewed by the naked eye, indicates sodium. Only in case a brilliant flame is observed should the presence of sodium be reported from this test alone.

#### Notes

1. Results of the flame test for sodium cannot be regarded too seriously, since most reagents contain sufficient sodium to give the flame coloration. However, a brilliant flame which persists for several seconds usually is evidence of a large quantity of the element. The flame test for potassium is more reliable, and of about equal sensitivity.

2. Other elements which might be found associated with sodium and potassium are lithium, rubidium, and caesium. The latter elements would precipitate with potassium in P 104. Their separation from potassium is a difficult procedure, and in general they are best detected by use of the spectrograph. Lithium resembles sodium in some properties; it is easily separated from sodium and potassium chlorides by extracting its chloride with organic solvents such as pyridine, amyl alcohol, etc.

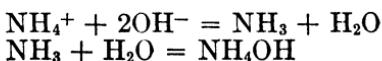
### P 107. Detection of Ammonium Ion.

To 5 drops of the original unknown solution add 0.5 ml. of NaOH. Boil the solution gently in a small test tube. Hold a moist piece of litmus paper near the mouth of the test tube, being careful not to touch the tube. If the litmus turns blue (caused by NH<sub>4</sub>OH), ammonium ion was present in the unknown.

Repeat the procedure, allowing the vapors to pass into 0.5 ml. of water. Add 3 drops of Nessler's reagent to the water. Orange-brown precipitate or color: NH<sub>2</sub>HgOHgI, the appearance of which confirms the presence of ammonium ion in the unknown.

#### Notes

1. Ammonium salts react with NaOH to liberate NH<sub>3</sub> which turns moist litmus blue by forming NH<sub>4</sub>OH.



With Nessler's reagent, which is a solution of  $K_2HgI_4$ , the reaction is:  $2HgI_4^- + H_2O + NH_3 \rightarrow NH_2HgOHgI + 3HI + 4I^-$ .

#### IDENTIFICATION OF ANION CONSTITUENTS

Prepared anion solution containing all anion constituents. Test portions as follows:

Add $HNO_3$ , $AgNO_3$ . P 201. <i>Precipitate:</i> Chloride Group. $AgCl$ , $AgBr$ , $AgI$ , $Ag_2S$ .	Add $HAc$ , $BaCl_2$ — $CaCl_2$ reagent. P 202. <i>Precipitate:</i> Sulfate Group. $BaSO_4$ , $BaSO_3$ , $BaCrO_4$ , $CaC_2O_4$ .	Add $MnCl_2$ — $HCl$ reagent. P 203. <i>Yellow-brown color:</i> Oxidizing Group. $NO_3^-$ , $NO_2^-$ , $CrO_4^-$ .	Add $H_2SO_4$ , $KMnO_4$ . P 204. <i>Decolorized:</i> Reducing Group. $Br^-$ , $I^-$ , $SO_3^-$ , $C_2O_4^-$ , $NO_2^-$ .
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All group tests positive; treat portions of anion solution to identify individual constituents:

Add $HAc$ , boil to remove $S^-$ . P 211. Add $HNO_3$ , $AgNO_3$ . P 212. <i>Precipitate:</i> $AgCl$ , $AgBr$ , $AgI$ . Analyze by P 213-217.	Add $HCl$ , neutralize, add $BaCl_2$ solution. P 221. <i>Precipitate:</i> $BaSO_4$ , $BaSO_3$ , $BaCrO_4$ , $BaC_2O_4$ . Analyze by P 222-224.	Special tests on original unknown, or on anion solution. Carbonate, by evolution of $CO_2$ , P 205. Sulfide, by evolution of $H_2S$ , P 206. Nitrite and nitrate, P 231. Borate, P 232.
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#### PREPARATION OF THE ANION SOLUTION

##### P 200. Treatment with Sodium Carbonate Solution.

If the sample (either in solution or a solid) is known to contain only  $K^+$ ,  $Na^+$ , and  $NH_4^+$  as cation constituents, this procedure may be omitted, and tests for anions begun directly with P 201.

Otherwise, treat about 50 mg. of the solid sample (or a portion of the solution containing about 50 mg. of total solids) in a casserole with 3 ml. of 3 *N*  $Na_2CO_3$  solution. Boil for 5 minutes, replacing water as it evaporates. (If the unknown was in solution, evaporation may be allowed and water added only to keep the volume about 3 ml.) Transfer precipitate and solution to a test tube and centrifuge. Reserve the "anion solution" for P 201; the residue for P 200-A.

**Notes**

1. Treatment with  $\text{Na}_2\text{CO}_3$  solution serves to transpose most insoluble salts (see p. 34), and to precipitate as hydroxides or carbonates cations whose presence would be undesirable in the anion analysis. The salts not affected by the treatment are: (1) most phosphates, (2) certain sulfides, such as  $\text{FeS}_2$ , (3) silver and mercurous halides. These constitute the residue which is tested by P 200-A.

**P 200-A. Analysis of Insoluble Residue.**

1. For phosphate. Transfer one-third of the residue to a test tube, add 0.5 ml. of  $\text{HNO}_3$ . Heat to boiling, cool, centrifuge. To 3 drops add several drops of  $(\text{NH}_4)_2\text{MoO}_4$  solution. Yellow precipitate:  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ .

2. For sulfide and halide. Treat the remainder of the residue with 0.5 ml. of  $\text{H}_2\text{SO}_4$  and several pieces of granular zinc. Test the evolved gas with lead acetate paper. Brown coloration:  $\text{PbS}$ . Allow the reaction to proceed until  $\text{H}_2\text{S}$  is no longer evolved. Centrifuge, remove the solution, and treat by P 201. If the test is positive, proceed directly to the analysis of the chloride group, P 212.

**Notes**

1. Most phosphates dissolve in  $\text{HNO}_3$ , at least partially, forming  $\text{HPO}_4^{2-}$ . The test is sensitive and characteristic.

2. For reactions of silver halides and zinc, see p. 100.

**PRELIMINARY TESTS FOR ANION CONSTITUENTS****P 201. Detection of the Chloride Group.**

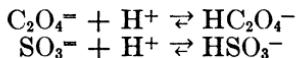
To 5 drops of anion solution, which has been neutralized with  $\text{HNO}_3$ , add an equal volume of water, 3 or 4 drops of  $\text{AgNO}_3$ , and 4 drops of  $\text{HNO}_3$ . Heat nearly to boiling. Precipitate:  $\text{AgCl}$ ,  $\text{AgBr}$ ,  $\text{AgI}$ ,  $\text{Ag}_2\text{S}$  (any or all).

**Notes**

1. A black precipitate with silver nitrate indicates sulfide; yellow, iodide; light yellow, bromide; white, chloride.

2. Sulfide may be found in P 206, yet not precipitated in the group test. This arises from the fact that upon acidification of the anion solution with  $\text{HNO}_3$ , the  $\text{S}^{2-}$  may be converted to  $\text{H}_2\text{S}$ , which escapes, or is oxidized to free sulfur.

3. The solution must be distinctly acid in testing for the chloride group, otherwise  $\text{Ag}_2\text{C}_2\text{O}_4$  or  $\text{Ag}_2\text{SO}_3$  will precipitate. By means of the reactions



the concentrations of  $\text{C}_2\text{O}_4^{2-}$  and  $\text{SO}_3^{2-}$  are lowered to such a value that precipitation is less likely. Heating serves to assist in dissolving any  $\text{Ag}_2\text{C}_2\text{O}_4$  or  $\text{Ag}_2\text{SO}_3$  that may have precipitated. If a positive test is obtained for the chloride group, yet in the subsequent analysis no ions of the chloride group are found, and large amounts of either or both of the above ions are found, they have probably interfered.

### P 202. Detection of the Sulfate Group.

To 5 drops of the anion solution add an equal volume of water. Add acetic acid until the solution is acid to litmus, then 2 drops in excess. Add 0.5 ml. of the mixed  $\text{BaCl}_2$ – $\text{CaCl}_2$  solution, heat nearly to boiling, and allow to stand for at least 10 minutes. Precipitate:  $\text{BaSO}_4$ ,  $\text{BaSO}_3$ ,  $\text{BaCrO}_4$ ,  $\text{CaC}_2\text{O}_4$  (any or all).

#### Notes

1. Sulfate, sulfite, and chromate are precipitated as the barium salts, while oxalate is precipitated by the calcium. Precipitation of barium oxalate is incomplete under the conditions specified. The solution is kept weakly acid to avoid forming  $\text{HCrO}_4^-$  and  $\text{HSO}_3^-$ , the presence of which would hinder precipitation of  $\text{BaCrO}_4$  and  $\text{BaSO}_3$ .

### P 203. Detection of the Oxidizing Group.

To 5 drops of the anion solution add 0.5 ml. of a saturated solution of  $\text{MnCl}_2$  in concentrated HCl. Heat nearly to boiling. Yellowish to dark brown color:  $\text{MnCl}_3$ .

#### Notes

1. With small quantities of oxidizing ions this test may fail. A comparison test should always be made using distilled water.

### P 204. Detection of the Reducing Group.

Place 2 or 3 drops of the anion solution on a spot plate depression; place in an adjacent position the same amount of

distilled water. Add 2 drops of  $H_2SO_4$  to each, then 1 drop of .001 *N*  $KMnO_4$  to each. If the color persists in each, the reducing group is absent. If the unknown decolorizes the  $KMnO_4$ , add several drops more of the reagent. A yellow color may be due to  $I_2$ . If observed, transfer the solution to a test tube, add 2 drops of  $CCl_4$ , shake. Purple color in  $CCl_4$  layer:  $I_2$ . (If the  $KMnO_4$  is decolorized by the distilled water, a contamination is present. Clean the spot plate, get fresh water, etc., and repeat the test.)

#### P 205. Detection of Carbonate.

If the original unknown is a solution, treat 5 drops in a 75 mm. test tube with  $Br_2$  water dropwise until the solution has a yellow color. Add HCl until distinctly acid; if a gas is evolved, it may be  $CO_2$ . Dip a nichrome wire loop in  $Ba(OH)_2$  solution, holding the drop over the test tube. Immediate appearance of turbidity in the drop:  $BaCO_3$ .

If the unknown is a solid, treat 5 to 10 mg. in a test tube with 5 drops of water, then treat with  $Br_2$  water and continue the test as above.

#### Notes

1. If the solution of the original unknown is acid, the test for carbonate need not be made. (Why?) Solid unknowns must obviously be tested prior to the sodium carbonate treatment for transposing the anions.

2. If  $SO_3^{2-}$  is present, it is oxidized to  $SO_4^{2-}$  by the bromine; otherwise  $SO_2$  would be liberated upon acidification, giving the reaction  $Ba(OH)_2 + SO_2 \rightarrow BaSO_3 \downarrow + H_2O$  which would make the test for  $CO_3^{2-}$  inconclusive.  $CO_2$  from the air slowly causes the  $Ba(OH)_2$  drop to become turbid, hence the initial observation is of importance.

#### P 206. Detection of Sulfide.

Treat 5 drops of the original unknown solution (or 5 to 10 mg. of the solid unknown) with several drops of dilute HCl; heat gently. Hold a strip of paper moistened with  $Pb(Ac)_2$  solution over the test tube. Darkening of the paper:  $PbS$ .

**P 211. Removal of Sulfide.**

If sulfide was found present in P 206, it must be removed before proceeding with the analysis of the chloride group. Acidify 5 drops of the anion solution with HAc, heat gently. Hold a piece of filter paper moistened with  $\text{PbAc}_2$  solution over the mouth of the test tube, and continue heating until  $\text{H}_2\text{S}$  is no longer evolved. In some cases it may be necessary to add 2 or 3 drops more of HAc. Avoid heating longer than necessary. Treat the solution by P 212.

**P 212. Precipitation of Chloride, Bromide, and Iodide.**

To the solution from P 211 add 4 drops of  $\text{HNO}_3$ , then  $\text{AgNO}_3$  dropwise until precipitation is complete. Heat almost to boiling, centrifuge, and discard the solution. Treat the precipitate by P 213.

**P 213. Separation of Chloride.**

Treat the precipitate from P 212 with 1 ml. of Miller's reagent, heating almost to boiling. Stir well, and allow the solution to stand for several minutes. Centrifuge, reserving the solution for P 214, the precipitate for P 215.

**Notes**

1. Miller's reagent is composed of  $\text{AgNO}_3$ ,  $\text{KNO}_3$ , and  $\text{NH}_4\text{OH}$ , the concentrations of which are so adjusted as to dissolve  $\text{AgCl}$ , but not  $\text{AgBr}$  or  $\text{AgI}$ . The action of the reagent in dissolving  $\text{AgCl}$  may be rather slow, and some  $\text{AgCl}$  may remain undissolved. This, however, does not interfere with the test for chloride, or with subsequent tests.

**P 214. Confirmation of Chloride.**

Acidify the solution from P 213 with  $\text{HNO}_3$ . White precipitate:  $\text{AgCl}$ . Centrifuge the precipitate, discarding the solution. Add 0.5 ml. of 12 *N* HCl and heat.  $\text{AgCl}$  will dissolve (forming  $\text{HAgCl}_2$ ), and reprecipitate slowly upon cooling the solution.

**P 215. Separation of Bromide.**

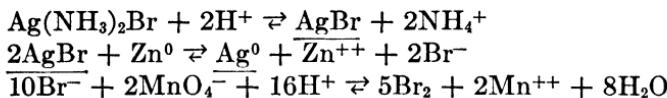
Treat the precipitate from P 213 with 0.5 ml. of  $\text{NH}_4\text{OH}$ , heating to boiling for 15 to 20 seconds. Centrifuge, treat the residue by P 217, the solution by P 216.

**P 216. Confirmation of Bromide.**

Neutralize the solution from P 215 with  $\text{HNO}_3$ . Yellow precipitate:  $\text{AgBr}$ . Centrifuge, discarding the solution. To the precipitate add 3 drops of  $\text{H}_2\text{SO}_4$ , 5 drops of water, and several small pieces of zinc. Allow the reaction to proceed for about 1 minute, then transfer several drops to a clean test tube. Treat with 2 drops of .001  $N$   $\text{KMnO}_4$  solution and 2 drops of  $\text{H}_2\text{SO}_4$ . Add 1 ml. of  $\text{CS}_2$  and shake. Orange color in the  $\text{CS}_2$ :  $\text{Br}_2$ .

**Notes**

1. The reactions involved in the above procedure are:



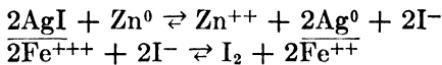
Some  $\text{AgCl}$  may have been retained in the mixed  $\text{AgBr}$ - $\text{AgI}$  precipitate. It will undergo the same reactions as  $\text{AgBr}$  except the last.

**P 217. Confirmation of Iodide.**

The precipitate from P 215 consists mainly of  $\text{AgI}$ , plus some  $\text{AgBr}$  which was not dissolved by the  $\text{NH}_4\text{OH}$ . Add 3 drops of  $\text{H}_2\text{SO}_4$  and 3 drops of water to the precipitate, then several small pieces of zinc. After allowing the reaction to proceed for a minute, remove several drops of the solution and add to them 1 drop of  $\text{Fe}(\text{NO}_3)_3$  solution. Add 1 ml. of  $\text{CCl}_4$  and shake. Purple color in the  $\text{CCl}_4$  layer:  $\text{I}_2$ .

**Notes**

1. The reactions involved are:



## SULFATE GROUP

### P 221. Precipitation of the Sulfate Group.

Acidify 0.5 ml. of the anion solution with HCl, then make just basic with NH<sub>4</sub>OH, using methyl orange if the solution is colorless; otherwise, litmus. Add BaCl<sub>2</sub> solution dropwise until precipitation is complete. Centrifuge the precipitate; wash once with 0.5 ml. water. Discard solution and washings. Treat precipitate by P 222.

#### Notes

1. The solution should be neutral before precipitation in order that SO<sub>3</sub><sup>-</sup> and CrO<sub>4</sub><sup>-</sup> will not escape detection by being present as HSO<sub>3</sub><sup>-</sup> and HCrO<sub>4</sub><sup>-</sup>.

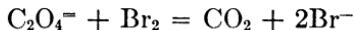
### P 222. Separation and Detection of Sulfate and Sulfite.

To the precipitate from P 221, add 0.5 ml. water and 0.5 ml. of HCl. Stir well and heat gently (without boiling). A white residue: BaSO<sub>4</sub>. In the absence of SO<sub>4</sub><sup>-</sup>, the precipitate dissolves completely. Centrifuge any precipitate, and to the solution add a slight excess of bromine water. If methyl orange has been used in P 221 in adjusting the acidity, bleaching of the color of the indicator will tell when sufficient bromine has been added. A white precipitate of BaSO<sub>4</sub> indicates that SO<sub>3</sub><sup>-</sup> was originally present. Centrifuge the precipitate and treat the solution by P 223. Discard all other precipitates.

#### Notes

1. The precipitate from P 222 consists of barium sulfate, and the barium salts of the weak acids H<sub>2</sub>SO<sub>3</sub>, H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, and H<sub>2</sub>CrO<sub>4</sub>. Upon addition of HCl, the ions SO<sub>3</sub><sup>-</sup>, C<sub>2</sub>O<sub>4</sub><sup>-</sup>, and CrO<sub>4</sub><sup>-</sup>, which are in equilibrium with the solid salts, are converted into HSO<sub>3</sub><sup>-</sup>, HC<sub>2</sub>O<sub>4</sub><sup>-</sup>, and HCrO<sub>4</sub><sup>-</sup>. Thus one of the products of the equilibrium BaSO<sub>3</sub> ⇌ Ba<sup>++</sup> + SO<sub>3</sub><sup>-</sup>, etc., is removed, and the precipitates dissolve. BaSO<sub>4</sub> alone is unaffected.

2. Bromine water oxidizes  $\text{SO}_3^{2-}$  to  $\text{SO}_4^{2-}$ , in which form it is precipitated from the strongly acid solution by the large excess of barium ions already present. The treatment with  $\text{Br}_2$  must not be unnecessarily prolonged, otherwise the reaction



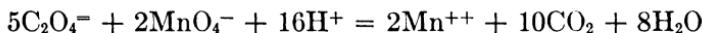
may take place to such an extent as to make the subsequent test for oxalate less conclusive.

### P 223. Detection of Oxalate.

To the solution from P 222 add 0.5 ml. of 1 *M*  $\text{NH}_4\text{Ac}$  and 0.5 ml. of  $\text{CaCl}_2$ . Allow the solution to stand for 15 minutes. White precipitate:  $\text{CaC}_2\text{O}_4$ . Centrifuge the precipitate; if the solution is colorless, discard; otherwise, treat by P 224. To the calcium precipitate add 0.5 ml. of  $\text{H}_2\text{SO}_4$ , heat for 0.5 minute. To a drop of solution on a spot plate add 1 drop of dilute  $\text{KMnO}_4$ . Decolorization of the  $\text{KMnO}_4$  indicates the presence of oxalate ion. A comparison test should be run using  $\text{H}_2\text{SO}_4$  and distilled water.

#### Notes

1. Ammonium acetate is added to adjust the pH sufficient to a value sufficient for the formation of  $\text{HCrO}_4^-$ , thereby preventing precipitation of  $\text{CrO}_4^{2-}$  by the  $\text{CaCl}_2$ . The white precipitate of calcium oxalate which forms dissolves in  $\text{H}_2\text{SO}_4$  with the formation of slightly ionized oxalic acid. The test with  $\text{KMnO}_4$  depends on the reaction:



### P 224. Detection of Chromate.

If the solution from P 223 is yellow, indicating the probable presence of chromate, add to it 3 drops of concentrated  $\text{HCl}$ , 0.5 ml. of  $\text{H}_2\text{O}_2$ , and 0.5 ml. of ether. Shake well. Blue color in ether layer:  $\text{CrO}_6^-$ .

#### Notes

1. Hydrogen peroxide oxidizes chromates to perchromic acid ( $\text{CrO}_6^-$ ), a blue compound soluble in ether. The test is sensitive, and provides additional evidence beyond the yellow color of the solution.

## SPECIAL TESTS

### P 231. Detection of Nitrate and Nitrite.

Treat 0.5 ml. of the anion solution with  $\text{BaCl}_2$  until precipitation is complete if chromate has been found in P 224. Centrifuge and discard the precipitate; reserve the solution. Otherwise proceed directly with the unknown solution.

To 1 drop of the chromate-free solution on a spot plate add 1 drop of sulfanilic acid solution and 1 drop of  $\alpha$  naphthylamine solution. A red color indicates the presence of nitrite. As an additional test for nitrite, 2 drops of the unknown may be treated on a spot plate with 4 drops of HAc and 2 drops of 10 percent thiourea solution. Add, after 1 minute, 1 drop of HCl and 1 drop of  $\text{Fe}(\text{NO}_3)_3$  solution. Red color: ferric thiocyanate complex, an indication of nitrite. (Iodide interferes).

If the nitrite test is strongly positive, the presence of nitrate is highly probable, and a satisfactory test for it cannot be made. However, if the nitrite test indicates only a small amount of that ion to be present, a test for nitrate should be made.

To 5 drops of the unknown, prepared as above, add an equal volume of  $\text{FeSO}_4$  solution. Shake well. Add several drops of concentrated  $\text{H}_2\text{SO}_4$  carefully, allowing the acid to run down the side of the centrifuge tube. A brown ring at the junction of the two layers indicates the presence of nitrate.

In the absence of nitrite, a blue color obtained when a drop of the solution is added to 2 drops of diphenylamine sulfonic acid solution on a spot plate also indicates nitrate.

### Notes

1. Chromate is removed before conducting the tests, since its color may lead to inconclusive results. Chromate and nitrite are not likely to be present together, at least not in acid solution.

2. The test for nitrite depends on the formation of a red dye with sulfanilic acid and  $\alpha$  naphthylamine. The test is specific for nitrite in the presence of nitrate.

3. The second test for nitrite depends on the formation of thiocyanate ion from the thiourea.

**P 232. Detection of Borate.**

In case iodide, chromate, or nitrite have been found present, follow procedures A and B. In case these ions are absent, follow procedure B only.

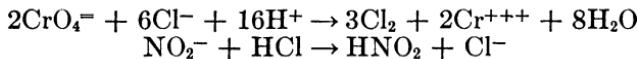
**A.** Evaporate 0.5 ml. of the  $\text{Na}_2\text{CO}_3$  anion solution to dryness in a casserole. Add carefully 5 drops of concentrated  $\text{HCl}$ , 1 drop of bromine water, and evaporate to dryness. Dissolve the residue in 0.5 ml.  $\text{H}_2\text{O}$ , add 5 drops of  $\text{Na}_2\text{CO}_3$ , and heat to boiling. Centrifuge, and treat the solution by B. Discard any precipitate.

**B.** Acidify 3 drops of the  $\text{Na}_2\text{CO}_3$  solution with  $\text{HAc}$ . Add 1 drop of this solution to 1 drop of turmeric reagent on a filter paper. Dry the paper, and to the spot add 1 drop of dilute (1 : 5)  $\text{NaOH}$ . A red-brown spot, turning dark blue or green on addition of the  $\text{NaOH}$ , indicates the presence of borate.

Acidify 0.5 ml. of the  $\text{Na}_2\text{CO}_3$  solution with  $\text{H}_2\text{SO}_4$  on a watch glass. Add 2 drops of concentrated  $\text{H}_2\text{SO}_4$  in excess. Add 0.5 ml. of methyl alcohol, stir well, and ignite the alcohol. A green flame is caused by boron.

**Notes**

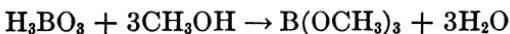
1. Nitrite, chromate, and ferric ion affect the color of turmeric, hence must be removed. Iodide must be removed since it may become oxidized to iodine, the color of which will obscure the test. In the evaporation with  $\text{HCl}$ , the following reactions take place:



The sodium carbonate is added to precipitate any  $\text{Cr}^{+++}$  that may have been produced.

2. The test with turmeric is highly sensitive. The addition of  $\text{NaOH}$  should not be omitted, however, as elements such as iron give a color with the reagent which is not, however, changed upon adding the base.

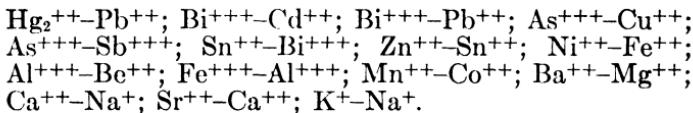
3. Borates react with methyl alcohol in the presence of  $\text{H}_2\text{SO}_4$  to form trimethyl borate,  $\text{B}(\text{OCH}_3)_3$ .



This compound when ignited burns with a green flame.

## GENERAL QUESTIONS

1. If silver and mercury (I) were incompletely precipitated in Group I, at what point would they appear in Group II? Write equations showing the tests in which these elements would interfere.
2. Account for a white precipitate obtained upon passing  $\text{H}_2\text{S}$  into the solution in the analysis of Group II.
3. Outline separations of the following ions in the fewest possible number of steps:  $\text{Zn}^{++}$ ,  $\text{Fe}^{+++}$ ,  $\text{Ni}^{++}$ ;  $\text{Zn}^{++}$ ,  $\text{Al}^{+++}$ ,  $\text{Mn}^{++}$ ;  $\text{Fe}^{+++}$ ,  $\text{Mn}^{++}$ ,  $\text{Cr}^{+++}$ .
4. Which of the elements in Groups IV and V may be commonly expected to occur in alloys?
5. What flame tests might be performed for Group IV elements? Do you think these especially reliable?
6. Outline a method for the separation and confirmation of  $\text{Ba}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{K}^{+}$  in the fewest possible number of steps.
7. Write equations for separating the following pairs of ions in the fewest possible steps.



8. List examples of complex ion formation in the scheme of cation analysis.
9. List the oxidation-reduction reactions made use of in the scheme of cation analysis.
10. Give solvents that will: (a) dissolve  $\text{AgI}$  but not  $\text{BaSO}_4$ , (b)  $\text{AgCl}$  but not  $\text{AgI}$ , (c)  $\text{PbCl}_2$  but not  $\text{PbCrO}_4$ , (d)  $\text{CuS}$  but not  $\text{HgS}$ , (e)  $\text{Al}(\text{OH})_3$  but not  $\text{Ni}(\text{OH})_2$ , (f)  $\text{Al}$  but not  $\text{Mg}$ , (g)  $\text{ZnS}$  but not  $\text{CuS}$ , (h)  $\text{SnS}_2$  but not  $\text{SnS}$ , (i)  $\text{Mg}(\text{OH})_2$  but not  $\text{Al}(\text{OH})_3$ , (j)  $\text{Ca}(\text{NO}_3)_2$  but not  $\text{Sr}(\text{NO}_3)_2$ .
11. A solution may contain  $\text{Pb}^{++}$ ,  $\text{Bi}^{+++}$ ,  $\text{Zn}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Sn}^{++}$ , and  $\text{Ba}^{++}$ , but no other cations. On the basis of the following experiments, state which ions are definitely shown to be present, which are definitely shown to be absent, and those concerning whose presence there is doubt.
  - (1)  $\text{NH}_4\text{OH}$  produces a precipitate which dissolves partially upon adding an excess.
  - (2) A solution of sodium sulfate produces a white precipitate.
  - (3) Sodium hydroxide produces a precipitate completely soluble in excess reagent.
12.  $\text{A}^{++}$ ,  $\text{B}^{++}$ ,  $\text{C}^{++}$ ,  $\text{D}^{++}$  represent four metallic ions which have the following properties:

- (1)  $A^{++}$  forms an amphoteric hydroxide whose solubility product is about  $10^{-30}$ .
- (2)  $B^{++}$  forms a hydroxide which is insoluble in water but which forms a complex with  $NH_3$ .
- (3) The solubility product of  $C(OH)_2$  is not exceeded in a solution of  $NH_4^+X^-$  and  $NH_4OH$ ; but the solubility product of  $D(OH)_2$  is exceeded in this solution.
- (4)  $C^{++}$  and  $D^{++}$  do not form amphoteric hydroxides. Making use of only the above properties, develop a reasonable method of separation indicating all the steps by general equations.

**13.** The hydroxide of  $N(OH)_2$  is insoluble in water.

- (1) If an equivalent amount of  $NaOH$  or  $NH_4OH$  is added to a solution containing  $N^{++}$  a precipitate is produced.
- (2) If an excess of  $NaOH$  is added to  $N^{++}$  a clear solution results.
- (3) If  $NH_4^+X^-$  is added to (2) and this solution boiled, a precipitate is formed.
- (4) If a mixture of  $NH_4^+X^-$  and  $NH_4OH$  is added to  $N^{++}$ , no precipitate is formed.
- (5) If an excess of  $NH_4OH$  is added to  $N^{++}$ , considerable precipitate remains and if the excess is removed by boiling, the precipitation is quantitative.

What property of  $N^{++}$  or  $N(OH)_2$  is illustrated in each of the above statements?

Summarize briefly the properties of  $N^{++}$  illustrated above.

**14.** An alloy was digested with dilute, then with concentrated  $HNO_3$ . A white precipitate (1) remained undissolved. The clear solution (2) was removed; the precipitate (1) was treated with dilute  $NaOH$ , in which all save a small portion dissolved. This small residue (3) was later found to be insoluble in several other acids and bases. The  $NaOH$  solution from precipitate (1) was acidified with  $HCl$ , and  $H_2S$  was passed in. A yellow precipitate (4) was obtained. The precipitate (4) was soluble in concentrated  $HCl$ , and in dilute  $NaOH$ . The clear solution (2), upon adjusting the acidity to 0.3 M and passing  $H_2S$ , gave a black precipitate, readily soluble in hot nitric acid (5). Addition of  $NaOH$  to the solution (5) gave a white precipitate, soluble in excess. The filtrate from the  $H_2S$  precipitation was made alkaline (without boiling) and a white precipitate was produced (6). Precipitate (6) was centrifuged off, and the filtrate (7) was discarded.

- (a) Of what did precipitate (1) consist?
- (b) Of what did residue (3) probably consist?
- (c) Why did precipitate (4) dissolve readily in  $NaOH$ ?
- (d) Which elements might have been in solution (5)?
- (e) Which element did solution (5) contain?
- (f) What might have been the content of precipitate (6)? Outline briefly a method to confirm your prediction.

(g) Which constituents of the alloy might have been discarded in filtrate (7)?

15. Boiling a solution of ferric acetate produces a precipitate of ferric hydroxide. Explain why.

16. A solution may contain any or all of the following ions. From the evidence given, state which ions are definitely present, which are definitely absent, and those whose presence is doubtful.

$H^+$ ,  $Cd^{++}$ ,  $Cu^{++}$ ,  $As^{+++}$ ,  $Fe^{+++}$ ,  $Ba^{++}$ ,  $Na^+$ ,  $OH^-$ ,  $CO_3^-$ ,  $S^-$ ,  $I^-$ ,  $C_2O_4^-$ ,  $SO_4^-$ .

- (1) The solution is colorless.
- (2)  $H_2S$  produces a yellow precipitate in the original solution.
- (3)  $NH_4OH$  produces a dark precipitate, partially soluble in excess.
- (4)  $(NH_4)_2SO_4$  produces a white precipitate.

**DETECTION OF CONSTITUENTS IN FERRO-ALLOYS**

Alloy partially dissolved (P 4). Evaporate with  $HClO_4$  (P 301).

<i>Residue:</i> $H_2SiO_3$ , $H_2WO_4$ . Analyze by P 302– P 304.	<i>Solution:</i> Extract with ether-hydrochloric acid mixture (P 305).
<i>Ether ex- tract:</i> $FeCl_3$ , $H_2MoO_4$ . Confirm Mo by P 306.	<i>Solution:</i> Adjust $[H^+]$ to 0.3 M, saturate with $H_2S$ gas (P 307).
<i>Precipi- tate:</i> $CuS$ , $As_2S_3$ , $MoS_3$ . Analyze by P 308– P 312.	<i>Filtrate:</i> Make alkaline with $NH_4OH$ , sat- urate with $H_2S$ gas (P 313).
<i>Solution:</i> $(NH_4)_3-$ $VS_4$ . Test by P 325.	<i>Precipi- tate:</i> Dissolve, add $NaOH$ – $Na_2O_2$ (P 313).
	<i>Precipi- tate:</i> $Fe(OH)_3$ , $MnO_2$ , $Co(OH)_3$ , $Ni(OH)_2$ , $Ti(OH)_4$ . Analyze by P 314– P 321.
	<i>Filtrate:</i> $NaAlO_2$ , $Na_2CrO_4$ . Acidify, make just basic (P 322).
	<i>Precipi- tate:</i> $Al(OH)_3$ . Confirm by P 323.
	<i>Solution:</i> Acidify, add $Pb(Ac)_2$ . <i>Yellow precipi- tate:</i> $PbCrO_4$ (P 324).

## SPECIAL PROCEDURES FOR FERRO-ALLOYS

Elements included: Fe, Co, Ni, Mn, Al, Cr, As, Cu, Si, W, Mo, V, Ti.

### P 301. Precipitation of Silicic and Tungstic Acids.

To 1 to 2 ml. of a solution of the alloy prepared according to P 4, add 5 to 10 drops of 16 *N* HNO<sub>3</sub> and 10 drops of HClO<sub>4</sub>. Evaporate in a small casserole, stirring or rotating continuously, until dense white fumes of HClO<sub>4</sub> come off and a pasty mass remains. Continue fuming for several minutes but avoid evaporating to complete dryness. Cool and add 1 ml. of HCl. Heat gently to dissolve salts, at the same time stirring thoroughly with a rubber policeman. Transfer to a 7.5 cm. test tube, rinsing the casserole with a few drops of HCl. Centrifuge. Residue: P 302. Solution: P 305.

#### Notes

1. The evaporation with HNO<sub>3</sub> and HClO<sub>4</sub> serves the following purposes: arsenic, tungsten, molybdenum, and iron are oxidized to their highest valences; silicic and tungstic acids are made insoluble by dehydration at the high temperature of boiling HClO<sub>4</sub>; replacement of HCl and HNO<sub>3</sub> by HClO<sub>4</sub> prevents the formation of basic salts of iron and other elements which would be difficult to dissolve in the next step.

2. More than 10 drops of 6 *N* HClO<sub>4</sub> should not be used because the presence of large amounts of this acid would interfere with the extraction of iron and molybdenum in P 305.

**WARNING:** Avoid the use of HClO<sub>4</sub> for any purposes other than those specified here. An explosion may result from contact of HClO<sub>4</sub> with organic matter.

3. Fuming for several minutes is necessary to dehydrate the silicic acids and to remove the excess of HClO<sub>4</sub>. H<sub>2</sub>SiO<sub>3</sub> and H<sub>2</sub>WO<sub>4</sub> are appreciably soluble in dilute HCl (P 302) while SiO<sub>2</sub> and WO<sub>3</sub> are quite insoluble.

4. When the soluble salts have dissolved in the HCl, the solution should be clear (not turbid), the residue light-colored and flocculent.

**P 302. Separation of Silicon and Tungsten.**

Wash the residue from P 301 twice with 1 ml. portions of hot HCl. Centrifuge and add the washings to the solution obtained in P 301. Treat the residue with 2 to 5 drops of 15 N NH<sub>4</sub>OH. Stir thoroughly, add 1 ml. of H<sub>2</sub>O and then centrifuge. A residue, which may be colored due to contamination, indicates silica. Confirm by P 303. Test the solution for tungsten by P 304.

**Notes**

1. If the fuming (P 301) has been carried too far or if a large amount of molybdenum is present, the residue obtained at this point may be brown due to iron or molybdenum. Both of these can be removed by repeated treatments with hot HCl.

2. WO<sub>3</sub> dissolves readily in cold, 15 N NH<sub>4</sub>OH forming (NH<sub>4</sub>)<sub>2</sub>WO<sub>4</sub> while SiO<sub>2</sub> is quite insoluble.

**P 303. Confirmation of Silicon.**

Add to the well-washed residue from P 302, 3 drops of Na<sub>2</sub>CO<sub>3</sub> solution and warm gently for a few seconds. Acidify with HCl but avoid an excess. To the slightly acid solution add 2 drops of (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub> reagent and warm gently. Cool and add 2 drops of benzidine reagent and then 5 drops of NaAc. A blue color confirms silicon.

**Notes**

1. Warming the residue gently for a moment or two with Na<sub>2</sub>CO<sub>3</sub> dissolves sufficient silica to give a satisfactory confirmatory test. The treatment used here with Na<sub>2</sub>CO<sub>3</sub>, on the other hand, does not dissolve silica from the Pyrex test tube to cause interference. It is not necessary to remove the residue unless it is quite dark colored, indicating that it contains considerable iron resulting from faulty technique.

2. The chemistry of the confirmatory test is as follows: When a soluble silicate is heated with (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub> in acid solution, a silico-molybdate, H<sub>2</sub>SiO<sub>4</sub>·12MoO<sub>3</sub>·aq., is formed. Silico-molybdate acid oxidizes benzidine to a blue quinoid product and at the same time the molybdenum is reduced to the so-called molybdenum blue which appears to be molybdenyl molybdate, (MoO<sub>2</sub>)<sub>2</sub>MoO<sub>4</sub>.

**P 304. Detection and Confirmation of Tungsten.**

Acidify with HCl the ammoniacal solution obtained in P 302. Add a few drops of SnCl<sub>2</sub> and warm. A white pre-

cipitate on acidification indicates tungsten. A blue precipitate or solution on warming with  $\text{SnCl}_2$  and HCl confirms tungsten.

#### Notes

1. One mg. or more of tungsten gives a distinct turbidity or precipitate when the solution is acidified. A smaller amount will give no turbidity but can be detected by warming the solution after the addition of  $\text{SnCl}_2$ . The blue product is probably  $(\text{WO}_2)_2\text{WO}_4$ .

### P 305. Extraction of Iron and Molybdenum.

Evaporate the solution from P 301 almost to dryness in a small casserole. Add 1 ml. of HCl and transfer the solution to a 10 cm. test tube, rinsing the casserole with a few drops of HCl. Cool thoroughly and add an equal volume of the ether reagent. Mix well by shaking and then insert a clean cork stopper and shake vigorously for about 1 minute; then let the layers separate. Carefully pipette out the ether layer, transfer it to a 10 cm. test tube, and reserve for the detection of molybdenum by P 306. Repeat the extraction two or three times more until the ether layer is colorless or, at most, very light colored. Add the ether extracts to the first and reserve for P 306.

Place the tube containing the water solution in a water bath and heat to remove the ether. The volume should now be not greater than 1 ml. If greater, evaporate to about this volume and then carefully neutralize with  $\text{NH}_4\text{OH}$  disregarding any precipitate which may form at this point. Make the solution just acid with HCl and add *one* drop of 12 N HCl and treat by P 307.

#### Notes

1. Evaporation of most of the acid, including  $\text{HClO}_4$ , and the addition of 6 N HCl to the almost dry residue gives the most favorable acid concentration for the extraction of iron and molybdenum with the ether-hydrochloric acid reagent. The solubility of  $\text{FeCl}_3$  and  $\text{H}_2\text{MoO}_4$  in ether reaches a maximum in 6 N HCl and decreases rapidly in HCl solutions of higher and lower concentrations. Ether saturated with HCl is used rather than ether alone

in order to prevent removal of HCl from the water layer during the extraction process.

From a solution 6 *N* in HCl and containing 90 mg. of ferric iron per ml., three or four extractions with equal volumes of the ether-HCl reagent will remove all but a few hundredths of a milligram of the iron. From a similar solution containing up to 10 to 15 mg. of molybdenum as  $H_2MoO_4$ , four extractions will reduce the amount of molybdenum to less than 0.1 mg. With amounts of molybdenum running as high as 20 to 30 mg. per ml., four extractions will remove most of the molybdenum but three or four additional extractions would be necessary to remove it completely. Complete removal is not necessary and provision is made in P 312 to recover any molybdenum which may be carried into Group IIB.

### P 306. Detection of Molybdenum.

Place the test tube containing the combined ether extract in a water bath and evaporate the ether. Add 1 to 2 drops of HCl and about 10 drops of water. Cool and then pour this solution all at once into a 10 cm. test tube containing 5 to 10 drops (an excess) of 15 *N*  $NH_4OH$ . Mix thoroughly. If the mixture is quite thick due to the presence of much  $Fe(OH)_3$ , add a few drops more of water, stir and then centrifuge. Pipette out the solution and just acidify it with HCl. Apply one or both of the following tests to portions of this solution. Discard the precipitate of  $Fe(OH)_3$ .

(a) *Thiocyanate Test.* Place 1 to 2 drops of the solution on a spot plate, add 1 to 2 drops of  $NH_4CNS$  and then a few particles of 20-mesh zinc. A deep red color forming around the zinc confirms molybdenum.

(b) *Thiosulfate Test.* Add to a few drops of the solution in a test tube 2 to 3 drops of NaAc and then 2 to 3 drops of  $Na_2S_2O_3$ . A blue color appearing in a few minutes indicates molybdenum. Finally, add a few drops of 12 *N* HCl. A red-brown precipitate confirms molybdenum.

### Notes

1. The acid solution is poured into the  $NH_4OH$  in order to keep the latter in excess at all times. In this way the formation of basic iron salts and the co-precipitation of molybdenum is largely avoided. If the solution is turbid after centrifuging, it is likely that too little

$\text{NH}_4\text{OH}$  was used. In the case of a turbid solution it is best to dissolve the precipitate in the smallest amount of  $\text{HCl}$  and pour it again into an excess of  $\text{NH}_4\text{OH}$ .

2. A red color appearing after the addition of  $\text{NH}_4\text{CNS}$ , but before the addition of zinc, indicates that some  $\text{Fe}(\text{OH})_3$  was transferred with the solution. In this case discard the test and reprecipitate the iron in the main portion of the solution with  $\text{NH}_4\text{OH}$  and remove it by centrifuging. Apply the thiocyanate test to the solution.

3. The deep red color produced, when a solution of an alkali molybdate acid with about 2  $N$   $\text{HCl}$  and containing  $\text{SCN}^-$  is treated with  $\text{SnCl}_2$  or  $\text{Zn}$ , is probably  $\text{MoO}(\text{SCN})_3$  or  $\text{Mo}(\text{OH})_2(\text{SCN})_3$ . It has recently been established that the molybdenum is in the pentavalent state and that the ratio  $\text{Mo} : \text{SCN}$  is 1 : 3.\*

4.  $\text{Na}_2\text{S}_2\text{O}_3$  added to a solution of an alkali molybdate, slightly acidified, gives a blue precipitate and a blue-colored solution, probably molybdenum blue. See P 303, Note 2. The red-brown precipitate which forms after strongly acidifying is probably a mixture of molybdenum sulfides.

### P 307. Precipitation of Group II.

Saturate with  $\text{H}_2\text{S}$  the cold solution prepared in P 305 and then place the tube in a water bath near the boiling point and continue to pass in  $\text{H}_2\text{S}$  for several minutes. Centrifuge and save the precipitate for P 308. If molybdenum is known to be absent, treat the solution by P 313. If molybdenum may be present, further treatment is necessary in order to insure its complete precipitation with the rest of Group II.

In this case transfer the solution to a casserole, boil out the  $\text{H}_2\text{S}$ , add a few drops of 16  $N$   $\text{HNO}_3$ , and evaporate nearly to dryness. Take up with 6  $N$   $\text{HCl}$ , again adjust the acidity as in P 305 and repeat the treatment with  $\text{H}_2\text{S}$  as given in the first paragraph of this procedure. Combine the two precipitates obtained with  $\text{H}_2\text{S}$  and treat by P 308. Treat the solution by P 313.

### Notes

1. The precipitation of Group II employed here is the same as was used in the general scheme (see P 21 and Notes) except when molybdenum is present. This element is completely precipitated

\* C. F. Hiskey and V. W. Meloche, J. Am. Chem. Soc. 62, 1565-74 (1940).

as the sulfide only by prolonged treatment with  $H_2S$  at elevated temperature and under pressure. In the semimicro treatment, at least, time can be saved by removing the sulfides precipitated by the treatment given in the first paragraph and then re-oxidizing to  $MoO_4^-$  the  $MoS_4^-$  present in the solution, and repeating the procedure given in the first paragraph.

### P 308. Separation of Groups II A and II B.

Add 1 to 5 drops of  $Na_2S$  reagent to the well-washed precipitate obtained in P 307. Stir well and warm gently. Add 10 drops of  $H_2O$ , stir and centrifuge. Save the residue for P 309. Carefully acidify the solution with  $HCl$ . Shake to coagulate the precipitate, and centrifuge. Discard the solution. If the residue is pure white, indicating sulfur, it may be discarded. If it is at all colored, treat it by P 310.

#### Notes

1. Washing removes Group III ions some of which would be precipitated by the strongly alkaline  $Na_2S$  reagent. Arsenic and molybdenum are the only Group II B elements likely to be present in ferro alloys.  $Na_2S$  reagent dissolves  $As_2S_5$  and  $MoS_3$  with the formation of the soluble thiosalts,  $Na_3AsS_4$  and  $Na_2MoS_4$ .

### P 309. Detection of Copper.

Dissolve the residue insoluble in  $Na_2S$  reagent by warming with dilute  $HNO_3$ . Remove any sulfur that is liberated and make the solution distinctly alkaline with  $NH_4OH$ . Blue color:  $Cu(NH_3)_4^{++}$ . Confirm by acidifying the solution with  $HAc$  and adding 1 drop of  $K_4Fe(CN)_6$ . If a precipitate is obtained continue the addition of  $K_4Fe(CN)_6$  until precipitation is complete. Red precipitate:  $Cu_2Fe(CN)_6$ .

#### Notes

1. Warm  $HNO_3$  is used here in order to take advantage of its oxidizing properties. The blue color of the  $Cu(NH_3)_4^{++}$  is usually sufficient evidence of the presence of copper, but the more sensitive confirmatory test with  $K_4Fe(CN)_6$  should be applied even though  $NH_4OH$  failed to produce a blue color. Furthermore, if  $Ni^{++}$  were here due to faulty technique, it would give a blue color but no red precipitate with  $K_4Fe(CN)_6$ .

**P 310. Separation of Arsenic and Molybdenum.**

Dissolve the residue, obtained in P 308 by the acidification of the  $\text{Na}_2\text{S}$  solution, by adding a few drops of 16 *N*  $\text{HNO}_3$  and warming. Remove precipitated sulfur, if necessary, and make the solution alkaline using 15 *N*  $\text{NH}_4\text{OH}$  in order to keep the volume as small as possible. Add an equal volume of magnesia reagent and cool thoroughly under tap water while stirring. Let stand at least 15 minutes unless a precipitate appears sooner. White crystalline precipitate:  $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ . Confirm by P 311. Treat the solution by P 312.

**Notes**

1. Concentrated  $\text{HNO}_3$  converts the sulfides of arsenic and molybdenum into  $\text{H}_3\text{AsO}_4$  and  $\text{H}_2\text{MoO}_4$ , respectively. Their separation depends upon the fact that  $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$  is only slightly soluble while molybdenum gives no precipitate with this reagent. In order to precipitate very small amounts of arsenic by this procedure, it is important that the volume be small, the solution cold, that a relatively large excess of magnesia reagent be used and that sufficient time be allowed for the  $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$  to crystallize. Stirring will hasten the crystallization.

**P 311. Confirmation of Arsenic.**

Wash the precipitate with small portions of 3 *N*  $\text{NH}_4\text{OH}$  until it is practically free from chloride (test). Add to the precipitate a few drops of  $\text{AgNO}_3$  to which 2 drops of HAc have been added. Red precipitate:  $\text{Ag}_3\text{AsO}_4$ .

**Notes**

1.  $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$  is appreciably soluble in water; therefore it is washed with  $\text{NH}_4\text{OH}$ . Chloride would decrease the delicacy of the test for arsenic since the solubility of  $\text{AgCl}$  is much lower than that of  $\text{Ag}_3\text{AsO}_4$ , the red precipitate. HAc dissolves the  $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ .

**P 312. Detection of Molybdenum.**

Neutralize the ammoniacal solution obtained in P 310 with HCl and add 1 drop in excess. Confirm by one of the tests given in P 306.

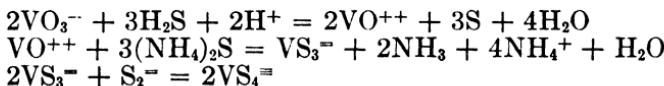
**P 313. Precipitation of Group III.**

Make the solution obtained at the end of P 307 strongly alkaline with  $\text{NH}_4\text{OH}$  and pass in  $\text{H}_2\text{S}$  for 5 minutes. Centrifuge and reserve the solution for the detection of vanadium in P 325. Wash the precipitated sulfides and hydroxides with dilute  $\text{NH}_4\text{OH}$  and then dissolve them by warming with a few drops of  $\text{HNO}_3$ . Make distinctly alkaline with  $\text{NaOH}$ ; cool and add  $\text{Na}_2\text{O}_2$  gradually in very small portions until gas bubbles continue to arise after thorough shaking. Heat in a water bath until the evolution of oxygen ceases. Centrifuge. Precipitate: P 314. Solution: P 322.

**Notes**

1. The ions of Group III are precipitated here as hydroxides and sulfides.  $\text{VO}_3^-$ , if present, in the original solution was reduced by  $\text{H}_2\text{S}$  in the acid solution to  $\text{VO}^{++}$  with the liberation of free sulfur. Free sulfur may also be present from the reduction of other ions by  $\text{H}_2\text{S}$ . When  $\text{H}_2\text{S}$  is passed into the ammoniacal solution,  $(\text{NH}_4)_2\text{S}_2$  and  $(\text{NH}_4)_2\text{S}_2$  are formed and  $\text{VO}^{++}$  is oxidized and converted into  $\text{VS}_4^-$ , giving a wine-red to an intense purple solution depending upon the amount of vanadium present.

Reactions:



The treatment with  $\text{NaOH}$  and  $\text{Na}_2\text{O}_2$  serves to separate chromium and aluminum from the other ions. The precipitate may contain  $\text{Fe}(\text{OH})_3$ ,  $\text{MnO}(\text{OH})_2$ ,  $\text{Ni}(\text{OH})_2$ ,  $\text{Co}(\text{OH})_3$ , and  $\text{TiO}(\text{OH})_2$ . Heating serves to decompose the excess  $\text{Na}_2\text{O}_2$ , expel oxygen, and convert orthotitanic acid,  $\text{Ti}(\text{OH})_4$ , which is partly precipitated from cold solutions and is somewhat soluble in excess  $\text{NaOH}$ , into metatitanic acid,  $\text{TiO}(\text{OH})_2$  which is much less soluble.

**P 314. Analysis of Group IIIA.**

Treat the precipitate obtained in P 313, which may contain hydroxides of Fe, Mn, Ni, Co, and Ti, with about 5 drops of 16 *N*  $\text{HNO}_3$ . Place the tube in a boiling water bath and add 1 drop of a saturated solution of  $\text{NaClO}_3$ . Continue heating for several minutes. Dark brown to black precipitate indicates manganese. Confirm by P 315. Treat solution by P 316.

**Notes**

1. Nitric acid dissolves all the hydroxides except that of manganese. Sodium chlorate insures re-precipitation of any manganese which may have been dissolved because of the presence of  $\text{HNO}_2$  in the  $\text{HNO}_3$ .

**P 315. Confirmation of Manganese.**

Dissolve the precipitate from P 314 by adding a few drops of  $\text{HNO}_3$  containing 1 to 2 drops of  $\text{H}_2\text{O}_2$ . Add a small amount of  $\text{NaBiO}_3$  and let stand. Purple color confirms manganese. For reactions see P 82 in the general scheme.

**P 316. Precipitation of Iron and Titanium.**

Pour the solution from P 314 into 10 drops (an excess) of 15 N  $\text{NH}_4\text{OH}$ . A red-brown precipitate indicates iron; a white precipitate indicates titanium. Centrifuge and wash the precipitate well with small portions of  $\text{NH}_4\text{OH}$ . Precipitate: P 317. Solution: P 320 and P 321.

**P 317. Separation of Iron and Titanium.**

Dissolve the precipitate from P 316 in a few drops of  $\text{H}_2\text{SO}_4$  and then add solid  $\text{NaHCO}_3$  in small portions until the evolution of  $\text{CO}_2$  ceases and the iron is precipitated. Centrifuge. Precipitate: P 318. Solution: P 319.

**Notes**

1. The pH of this solution, which is practically saturated with  $\text{NaHCO}_3$  and  $\text{H}_2\text{CO}_3$ , is sufficiently high to precipitate iron as  $\text{Fe}(\text{OH})_3$  but is too low to precipitate titanium. Since  $\text{Ti}(\text{OH})_4$  is also soluble in alkali carbonates,  $\text{Na}_2\text{CO}_3$ ,  $(\text{NH}_4)_2\text{CO}_3$ , the titanium may be present in this solution as a complex anion, for example as  $\text{Ti}(\text{CO}_3)_3^-$ .

**P 318. Confirmation of Iron.**

Dissolve the precipitate from P 316 in  $\text{HCl}$ . Add  $\text{NH}_4\text{CNS}$ . A deep red color confirms iron. See P 84.

**P 319. Confirmation of Titanium.**

Carefully acidify the  $\text{NaHCO}_3$  solution from P 316 with  $\text{H}_2\text{SO}_4$ . Add a few drops of  $\text{H}_2\text{O}_2$ . Yellow to red color confirms titanium.

**Notes**

1. The reaction of  $Ti^{++++}$  with  $H_2O_2$  is a very delicate test for this element. The color is yellow to red depending upon the concentration of titanium present. The composition of the product formed is still open to question but is said to be a pertitanic acid having the formula  $H_2TiO_4$  or  $H_4TiO_5$ .

**P 320. Detection of Nickel.**

To a portion of the solution from P 316 in a spot plate, add 2 to 3 drops of dimethylglyoxime. If a precipitate is not obtained immediately, add gradually a few drops of HAc before concluding that nickel is absent. Bright red precipitate indicates Ni. See P 85.

**P 321. Detection of Cobalt.**

To another portion of the solution from P 316 acidified with  $H_2SO_4$ , add solid  $NH_4CNS$  until the solution is nearly saturated. Add 1 ml. of amyl alcohol and shake well. A blue color in the alcohol layer confirms cobalt. See P 86.

As an alternative test for cobalt, another portion of the solution from P 316 may be acidified with HAc and to a drop of this solution on filter paper a drop of  $\alpha$  nitroso  $\beta$  naphthol added. A reddish brown spot indicates cobalt. See P 86.

**P 322. Separation of Aluminum and Chromium.**

Acidify the alkaline solution from P 313 taking care that the solution does not become hot during the neutralization process. Make the solution just alkaline with  $NH_4OH$ . White precipitate:  $Al(OH)_3$ . Heat to coagulate the precipitate and filter. Precipitate: P 323. Filtrate: P 324.

**P 323. Confirmation of Aluminum.**

Dissolve the precipitate from P 322 from the filter with a few drops of warm HCl. To the solution add 3 drops of  $NH_4Ac$  and 3 drops of aluminon reagent. Make the solution alkaline by the addition of  $(NH_4)_2CO_3$ , adding 2 to 3 drops in excess. Boil. A red precipitate confirms aluminum. See P 72.

**P 324. Confirmation of Chromium.**

Acidify the filtrate from P 322 with HAc, add 3 drops of  $\text{PbAc}_2$  and heat to boiling. Yellow precipitate confirms chromium. See P 73.

**P 325. Detection of Vanadium.**

Pour the ammoniacal solution obtained in P 313 into an excess of 1 *N* HCl. Dark brown precipitate indicates vanadium. Centrifuge and dissolve the precipitate in a little warm  $\text{HNO}_3$ . Boil to expel oxides of nitrogen. Cool and add a few drops of  $\text{H}_2\text{SO}_4$  and a drop or two (avoid an excess) of  $\text{H}_2\text{O}_2$ . A yellow to red color which is not extracted by ether nor decolorized by HF confirms vanadium.

**Notes**

1. Acidification of the thiovanadate solution causes the incomplete precipitation of  $\text{V}_2\text{S}_5$ .  $\text{H}_2\text{O}_2$  in acid solution (15 to 20 percent  $\text{H}_2\text{SO}_4$ ) forms the deep red pervanadic acid,  $\text{HVO}_4$ , with vanadates. The color is destroyed by an excess of  $\text{H}_2\text{O}_2$  but is not extracted by ether (distinction from chromium) nor is it decolorized by HF (distinction from titanium).

**TREATMENT OF ALLOYS CONTAINING A HIGH PERCENTAGE OF ALUMINUM**

The demand in recent years for strong, light, non-corrosive alloys has given impetus to the manufacture of a wide variety of alloys containing aluminum as a major constituent. Alone, aluminum lacks desirable qualities of hardness, ductility, and tensile strength, but does possess the desirable property of lightness and resistance to corrosion. This latter property is believed to result from the formation of a thin coating of oxide on the surface of the metal, thus protecting it against further reaction.

The addition of zinc to aluminum produces an alloy which has greater strength than pure aluminum, although about the same ductility. Addition of copper increases the rigidity, although at a loss of ductility. Since aluminum-zinc alloys

are easily corroded, they are commonly covered with a thin sheet of pure aluminum ("Alclad").

Magnesium when alloyed with aluminum produces materials that are stronger and more easily machined than aluminum itself. Magnalium is a common alloy of this type; it may contain 70 to 90 percent aluminum, the remainder being magnesium.

Duralumin is an alloy having about one-third the weight of steel, yet equal strength. It contains at least 95 percent aluminum, the remainder being made up of manganese, copper, magnesium, silicon, and iron. These last elements are frequently encountered in aluminum alloys and even in aluminum itself, since commercial aluminum (99.2 percent pure) contains traces of these elements.

From this it appears that the elements commonly encountered in the analysis of aluminum alloys are zinc, magnesium, copper, manganese, silicon, iron; tin and lead are occasionally present in small amount. Products may be encountered which contain large amounts of iron; these are probably samples of aluminum-plated steel. Their analysis does not come under the following sections, but rather under the analysis of special steels. Products of this type are prepared by dipping the steel in molten aluminum.

The directions which follow (P 401-P 405) are for dissolving alloys of this type, and for removing the large quantities of aluminum necessarily present prior to the detection of other constituents.

#### **P 401. Preparation of Solution. Removal of Silica.**

To 100 mg. of the alloy in a casserole add 1 ml. of concentrated HCl, several drops of water, and 5 drops of HClO<sub>4</sub>. Heat if necessary to dissolve the alloy; evaporate carefully to fumes of HClO<sub>4</sub>. As dryness is approached the crystallized salts may spatter, and care is necessary to avoid mechanical losses. Treat the residue with 0.5 ml. of HCl, plus sufficient water to dissolve completely the salts. Heat if nec-

essary. Transfer the solution to a test tube, including any residue which may remain in the casserole. A rubber policeman, such as used in quantitative analysis, is useful for this purpose. Centrifuge the solution; reserve the clear liquid for P 403. Wash any precipitate that may have separated with 5 drops of water plus 1 drop of HCl. Discard the washings. Test the precipitate for silica by P 303.

#### Notes

1. Aluminum alloys are readily soluble in a mixture of hydrochloric acid and perchloric acid. Nitric acid, a common solvent for many alloys, acts in such a way as to form a protective coating of aluminum oxide on aluminum alloys, thus rendering them inert. This phenomenon, known as passivity, is also shown to a certain extent by iron and cobalt. Aluminum alloys may also be decomposed by treatment with sodium hydroxide solution.

2. Perchloric acid is added to assist in the dehydration of silica, as well as to dissolve copper and other constituents of the alloy which are insoluble in HCl. An oxidizing acid, it might in larger amounts render the aluminum passive. It assists in preventing loss of  $\text{FeCl}_3$  by volatilization during the dehydration process.

3. The amount of silica obtained in the dehydration is generally small, and may indeed be entirely overlooked unless the directions are followed carefully. The silica is light in color and difficult to observe, hence the procedure for isolating and confirming it should be carried out whether or not a precipitate is observed.

#### P 402. Removal of Aluminum.

The solution from P 401, which should be about 2 ml. in volume, is cooled in ice water to less than 15° C. A rapid stream of HCl gas is then passed through the solution for 2 minutes. Add 2 ml. of ether and continue passage of the gas until a dense white precipitate forms, then for 2 minutes longer. Centrifuge and discard the precipitate. Treat the solution again with HCl gas; if additional precipitate is obtained, centrifuge and discard as before. Treat the solution by P 403.

#### Notes

1. As many constituents of aluminum alloys are present in small amounts, their detection would be rendered difficult in the presence

of large amounts of aluminum present in a 100 mg. sample. The procedure given here is effective in removing the aluminum without loss of other elements. It is essentially the method of Gooch and Havens\* which may under proper conditions be used for the quantitative precipitation of aluminum. The aluminum is precipitated as the hydrated chloride,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ .

2. The HCl gas may be prepared in a gas generator in which technical  $\text{H}_2\text{SO}_4$  drops onto table salt. The gas should be passed through a second bottle before use.

3. The second passage of HCl through the solution may result in the formation of more  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , which should be discarded. Some aluminum may still remain after the two precipitations with HCl, but gives no interference during the subsequent steps.

### P 403. Removal of Ether.

Evaporate the ether from the solution by holding the test tube in a beaker of hot water *in a good hood*. Transfer the remaining solution to a crystallizing dish, evaporate to near dryness. Add 3 drops of 12 N HCl and repeat. Dissolve the residue in 1 ml. of water, treat by P 21, starting with the third sentence.

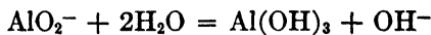
The analysis now proceeds according to the scheme of general cation analysis. In case beryllium may be present, the following procedure should follow P 62.

### P 404. Detection of Beryllium.

The solution from P 62 is neutralized with HCl until a permanent precipitate is almost formed. In case a slight precipitate does form, add 1 drop of NaOH. Boil the solution for 30 seconds. A white precipitate indicates beryllium.

#### Notes

1. In the sodium hydroxide solution obtained from P 62, aluminum and beryllium are present as aluminate ( $\text{AlO}_2^-$ ) and beryllate ( $\text{BeO}_2^-$ ) ions. Removal of the excess hydroxyl ions by addition of HCl tends to displace the equilibrium



\* Am. Jour. Sci. (4) 2, 416 (1898).

in the direction of  $\text{Al(OH)}_3$ , hence a precipitate may appear if too much acid is added. The point at which the hydroxides just remain in solution is sometimes called the "isoelectric point." Boiling the solution drives the reaction  $\text{BeO}_2^- + 2\text{H}^+ = \text{Be(OH)}_2$  to completion more readily than the corresponding reaction for aluminum. This might be expected, since aluminum shows a more acidic character than beryllium (i.e., is more amphoteric).

## APPENDIX

### TERMS AND DEFINITIONS

#### Weights.

A *gram molecular weight* (mol) is the molecular weight of a substance taken in grams. A *milligram molecular weight* (millimol) is one-thousandth of this quantity. *Example:* The molecular weight of sodium chloride is 58.5, therefore a mol of NaCl will be 58.5 grams, and a millimol 58.5 milligrams.

The *equivalent weight* of a substance depends on the reaction undergone by the substance. The equivalent weight of an acidic or basic substance is the number of grams of that substance which will contain, or react with, 1 gram atom of hydrogen. The equivalent weight of an oxidizing or reducing agent is the number of grams of the substance which oxidizes 1 gram atom of hydrogen, or produces the same reducing action as 1 gram atom of hydrogen. A *milliequivalent weight* is one-thousandth of an equivalent weight. *Examples:* Since  $\text{H}_2\text{SO}_4$  contains 2 gram atoms of hydrogen per mol, the equivalent weight will be one-half of the molecular weight, or 49. Since  $\text{KMnO}_4$  in acid solution produces the same oxidizing action as 5 gram atoms of hydrogen ion, the equivalent weight is one-fifth of the molecular weight.

#### Concentration of Solutions.

A *molar* solution contains 1 gram molecular weight (1 mol) of the solute per liter of solution. *Example:* One molar NaCl contains 58.5 grams of NaCl per liter of solution.

A *molal* solution contains 1 gram molecular weight of solute per 1000 grams of solvent. *Example:* One molal NaCl contains 58.5 grams of NaCl per 1000 grams of water. This method of expressing concentration is rarely used in practical work.

A *normal* solution contains 1 gram equivalent weight of solute per liter of solution. *Example:* One normal sulfuric acid contains 49 grams of  $\text{H}_2\text{SO}_4$  per liter.

The concentration of solutions is sometimes expressed on a *percentage* basis. This may be expressed as percent by weight, or percent by volume. In the former case, the percent is the number of grams of solute per 100 grams of solution; in the latter, the number of milliliters of solute per 100 ml. of solution. *Examples:* A 10 percent NaOH solution contains 10 grams of NaOH in 90 grams of water. A 10 percent alcohol solution contains 10 milliliters of alcohol in 100 ml. of solution.

### Miscellaneous Terms.

*Electrovalence* results from the transfer of electrons between atoms.

*Covalence* results from the sharing of electrons between atoms.

*Coordinate covalence* results from the donation of a pair of electrons by an ion or molecule to another ion or molecule.

A *strong electrolyte* is generally an electrovalent compound, completely dissociated in aqueous solution.

A *weak electrolyte* is generally a covalent compound, slightly dissociated in aqueous solution.

*Hydrolysis* is the reaction of a salt and water to form an acid and a base.

An *oxidant* (oxidizing agent) is a substance capable of removing electrons from another substance, thus becoming reduced.

A *reductant* (reducing agent) is a substance capable of losing electrons readily to another substance, thus becoming oxidized.

By *amphoteric* is meant the ability of a substance to react in either an acid or basic capacity.

## Review of Mathematical Operations

### Expressing Numbers. Exponents.

It is frequently convenient to express very large or very small numbers as decimal fractions multiplied by 10 raised to the proper power. This facilitates the handling of such numbers in certain mathematical operations.

#### EXAMPLES:

2,000,000 may be written as  $2 \times 10^6$

13,000 may be written as  $1.3 \times 10^4$

0.00017 may be written as  $1.7 \times 10^{-4}$

0.000000459 may be written as  $4.59 \times 10^{-7}$

The location of the decimal point is arbitrary, although it is easier to estimate the order of magnitude of the result of a calculation if the numbers are written with one figure at the left of the decimal point.

### Multiplication and Division of Exponentials.

$$(a \times 10^n)(b \times 10^m) = ab \times 10^{n+m}$$

#### EXAMPLES:

$$(10^2)(2 \times 10^4) = 2 \times 10^6$$

$$(3.2 \times 10^3)(3 \times 10^{-1.5}) = 9.6 \times 10^{1.5}$$

$$(a \times 10^n) \div (b \times 10^m) = \frac{a}{b} \times 10^{n-m}$$

#### EXAMPLES:

$$(10^2) \div (2 \times 10^4) = \frac{1}{2} \times 10^{-2} = 5 \times 10^{-3}$$

$$(3.2 \times 10^3) \div (3 \times 10^{-1.5}) = 1.07 \times 10^{4.5}$$

$$(a \times 10^n)^m = a^m \times 10^{nm}$$

#### EXAMPLES:

$$(4 \times 10^3)^3 = 64 \times 10^9 = 6.4 \times 10^{10}$$

$$(4 \times 10^{-3})^3 = 64 \times 10^{-9} = 6.4 \times 10^{-8}$$

$$\sqrt[m]{a \times 10^n} = \sqrt[m]{a} \times 10^{n/m}$$

#### EXAMPLE:

$$\sqrt[4]{2.7 \times 10^{-8}} = \sqrt[4]{27 \times 10^{-9}} = 3 \times 10^{-3}$$

**Logarithms.**

The common logarithm of a number is the power to which 10 must be raised to give that number. Thus, the logarithm of 100 is 2, since  $10^2 = 100$ .

A logarithm is composed of the characteristic and the mantissa. The characteristic is an integer, found by inspection, being one less than the number of figures at the left of the decimal point in the number in question. The mantissa is found from tables.

**EXAMPLES:**

Number	Characteristic of log	Mantissa (from Table)	Log of Number
30,000	4	0.4771	4.4771
300	2	0.4771	2.4771
3.00	0	0.4771	0.4771
1.00	0	0.0000	0.0000
0.3	-1 (9 ⋯ -10)	0.4771	9.4771 - 10 -1.4771
0.003	-3 (7 ⋯ -10)	0.4771	7.4771 - 10 -3.4771

Logarithms may be used for all types of multiplication and division.

$$\log (a)(b)(c) \cdots (n) = \log a + \log b + \log c \cdots + \log n$$

$$\log (a)^n = \log a + \log a \cdots = (n)(\log a)$$

**EXAMPLES:**

$$\log (3)(45)(235) = \log 3 + \log 45 + \log 235$$

$$= 0.4771 + 1.6532 + 2.3711 = 4.5014$$

$$(3)(45)(235) = \text{antilog } 4.5014$$

$$= 31,730$$

$$\log (25)^4 = 4(\log 25) = (4)(1.3979) = 5.5916$$

$$(25)^4 = \text{antilog } 5.5916$$

$$= 390,500$$

$$\log (a/b) = \log a - \log b$$

$$\log \sqrt[n]{a} = \frac{\log a}{n}$$

## EXAMPLES:

$$\begin{aligned}\log (456/556) &= \log 456 - \log 556 \\ &= 1.6590 - 1.7451 = 9.9139 - 10 \text{ (add and} \\ &\text{subtract 10 from the first number,} \\ &\text{making it } 11.6590 - 10; \text{ the indicated} \\ &\text{operation can then be performed).}\end{aligned}$$

$$\begin{aligned}456/556 &= \text{antilog } 9.9139 - 10 \\ &= 0.8201\end{aligned}$$

$$\begin{aligned}\log \sqrt[5]{30} &= \frac{\log 30}{5} = \frac{1.4771}{5} = 0.2954 \\ \sqrt[5]{30} &= \text{antilog } 0.2954 \\ &= 1.974\end{aligned}$$

## LIST OF APPARATUS

### NON-RETURNABLE

1 length glass rod, 75 cm.  $\times$  4 mm.  
1 length glass tubing, 75 cm.  $\times$  6 mm.  
2 towels  
1 sponge  
1 box matches  
1 box labels  
1 No. 5 2-hole rubber stopper  
1 spatula  
1 funnel brush  
1 test tube brush  
1 tube red litmus paper  
1 tube blue litmus paper  
1 package spot test paper  
10 sheets hardened filter paper  
1 2" length Nichrome or platinum wire

### RETURNABLE

6 droppers with bulbs  
12 test tubes, 9 mm.  $\times$  75 mm.  
12 test tubes, 13 mm.  $\times$  100 mm.  
1 600 ml. Pyrex beaker  
1 400 ml. Pyrex beaker  
1 250 ml. Pyrex beaker  
2 100 ml. Pyrex beakers  
2 30 ml. Pyrex beakers  
1 graduated cylinder, 10 ml.  
1 graduated cylinder, 100 ml.  
1 spot plate  
1 short stem funnel, about 1 $\frac{3}{4}$ " dia.  
1 filter flask, 250 ml.  
1 10 ml. Erlenmeyer flask  
1 casserole, 30 ml.  
2 watch glasses, 2"  
1 test tube block  
10 Barnes dropping bottles, or screw cap dropping bottles  
1 micro burner  
2 centrifuge tubes, 75 mm.  
2 crucibles, 30 ml.  
1 500 ml. flat bottom flask  
1 test tube holder  
1 hydrogen sulfide generator set

TABLE V—Continued

No.	LOGARITHMS									Proportional Parts									
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8082	8089	8096	8075	8082	8089	8096	8102	8109	8116	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8766	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

## REAGENTS USED IN SEMIMICRO QUALITATIVE ANALYSIS

Each student should have a set of the common reagents at his desk (see p. 53). The less frequently used reagents may be dispensed from the side shelves. Several sets of these reagents may be placed in the laboratory; it has been found that one set of reagents will serve fifteen to twenty students. The liquid reagents should be placed in 100, 250, or 500 ml. bottles, depending on the quantity of reagent used, fitted with droppers.

The reagents are listed in the approximate order of use in the laboratory work. Liquid reagents and solid reagents are listed separately.

### Liquid Reagents.

Nitric acid, conc., 16 molar.

Nitric acid, dilute, 6 molar. 380 ml. conc.  $\text{HNO}_3$  diluted to 1 liter.

Hydrochloric acid, conc., 12 molar.

Hydrochloric acid, dilute, 6 molar. Dilute 520 ml. of conc.  $\text{HCl}$  to 1 liter.

Sulfuric acid, dilute, 3 molar. Mix conc.  $\text{H}_2\text{SO}_4$  and water 1 : 5.

Ammonium hydroxide, conc., 15 molar.

Ammonium hydroxide, dilute, 6 molar. Mix 400 ml. conc.  $\text{NH}_4\text{OH}$  dilute to 1 liter.

Acetic acid, dilute, 6 molar. Mix 350 ml. of glacial acetic acid with 650 ml. water.

Sodium carbonate, 3 normal. 160 g. per liter of water.

Ammonium chloride, 3 normal. 160 g. per liter.

Potassium chromate, 1.5 molar. 290 g. per liter.

Bromine water. Saturated solution of bromine in water.

Sodium sulfide-sodium hydroxide reagent. Dissolve 480 g. of  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  and 40 g. of  $\text{NaOH}$  in 1 liter of water.

Stannous chloride reagent. 115 g. of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  dissolved in 170 ml. conc.  $\text{HCl}$ , diluted to 1 liter. Keep metallic tin in reagent bottles.

Ammonium acetate, 3 normal. 250 g. per liter.

Potassium ferrocyanide, 1 normal. 105 g. per liter.

Salicylaldoxime, 1 percent. Dissolve 1 g. of salicylaldoxime in 10 ml. ethyl alcohol, dilute to 100 ml. with water.

Potassium cyanide, 1 molar. 65 g. per liter.

Magnesia reagent. Dissolve 130 g. of  $Mg(NO_3)_2 \cdot 6H_2O$  and 240 g. of  $NH_4NO_3$  in water, add 35 ml. dilute  $NH_4OH$ , dilute to 1 liter.

Silver nitrate, 1 normal. 170 g. per liter.

Mercuric chloride, 0.2 normal. 25 g. per liter.

Ammonium molybdate reagent. Dissolve 90 g. of ammonium molybdate in 100 ml. dil.  $NH_4OH$ , add 240 g.  $NH_4NO_3$ , dilute to 1 liter.

Bismuth nitrate, 0.1 molar. Add 31 ml. conc.  $HNO_3$  to 49 g. of  $Bi(NO_3)_3 \cdot 5H_2O$ , dilute slowly to 1 liter.

Formate buffer. Dissolve 2.8 g. of sodium formate in 100 ml. of 23 molar formic acid.

Acrolein. Dissolve 0.5 ml. of acrolein in 100 ml. of water.

Aluminon reagent. Dissolve 0.5 g. per 100 ml.

Ammonium carbonate, 3 molar. 340 g. per liter.

Lead acetate, 1 normal. 190 g. per liter.

Sodium chlorate. Saturated aqueous solution.

Hydrogen peroxide, 3 percent.

Ammonium thiocyanate, 1 molar. 76 g. per liter.

Dimethylglyoxime, 1 percent. Dissolve 1 g. in 100 ml. ethyl alcohol.

Amyl alcohol (iso).

Alpha nitroso beta napthol. Dissolve 10 g. in 500 ml. of 50 percent acetic acid (heat). Filter when cool.

Methyl alcohol (wood alcohol).

Ammonium oxalate, 0.3 molar. 44 g. per liter.

Disodium hydrogen phosphate, 0.3 molar. 115 g. per liter.

Ethyl alcohol, 95 percent.

Ammonium sulfate, 1 molar. 120 g. per liter.

Magneson reagent (*p*-nitrobenzene azo resorcinol). Prepare 0.1 percent solution in 1 percent NaOH.

Sodium cobaltinitrite. Dissolve 230 g.  $\text{NaNO}_2$  in 500 ml. water, add 165 ml. 6 normal acetic acid, 30 g. cobalt nitrate. Allow to stand 12 hours, filter, dilute to 1 liter.

Zinc uranyl acetate. Dissolve 10 g. of uranyl acetate in 65 ml. water containing 6 g. of 30 percent acetic acid. Prepare a second solution of 30 g. of zinc acetate in 65 ml. of water containing 3 g. of acetic acid (30 percent). Heat to assist in dissolving the solids. Mix the solutions, cool to 20°. Filter after several hours' standing.

Nessler's reagent. Dissolve 8 g. of  $\text{KI}$  and 11.5 g. of  $\text{HgI}_2$  in 45 ml. of water. Add 50 ml. of dilute  $\text{NaOH}$ . Keep in dark bottles.

Barium chloride—calcium chloride reagent. Mix 1 normal  $\text{BaCl}_2$  (120 g. per liter) with 1 normal  $\text{CaCl}_2$  (110 g. per liter) in ratio 1 : 3 by volume.

Manganous chloride in hydrochloric acid. Saturated solution in conc.  $\text{HCl}$ .

Potassium permanganate, 0.001 normal. 32 mg. per liter.

Barium hydroxide. Shake 60 g.  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  with a liter of water; filter.

Miller's chloride reagent. 1.7 g.  $\text{AgNO}_3$  and 25 g.  $\text{KNO}_3$  in 500 ml. water. Add 17 ml. 15 normal  $\text{NH}_4\text{OH}$ , dilute to 1 liter.

Carbon disulfide.

Carbon tetrachloride.

Ether.

Alpha napthylamine. Boil 3 g. of alpha napthylamine with 300 ml. of water; decant, mix solution with 300 ml. of glacial acetic acid.

Sulfanilic acid. Dissolve 10 g. in 1 liter of 30 percent acetic acid, warming if necessary.

Thiourea, 10 percent solution.

Ferric nitrate, 1 normal. 135 g.  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  per liter.

Ferrous sulfate. 150 g.  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in 1 liter of water containing 10 ml. conc.  $\text{H}_2\text{SO}_4$ . Add pieces of metallic iron to keep solution reduced.

Diphenyl amine. Add 10 mg. diphenylamine to 10 ml. conc.  $H_2SO_4$ . Dilute carefully to 100 ml. with dil.  $H_2SO_4$ .

Turmeric. Saturated solution in ethyl alcohol.

### Solid Reagents.

Antimony.	Sodium peroxide.
Tin.	Sodium bismuthate.
Potassium cobalticyanide paper.*	Ammonium thiocyanate. Zinc.

### Special Reagents for Ferro-Alloys and Aluminum Alloys.

(In addition to the above.)

Perchloric acid, 60 percent.

Benzidine reagent. 0.05 g. benzidine (or the hydrochloride) is dissolved in 10 ml. acetic acid (glacial), and the solution diluted to 100 ml.

Sodium acetate, 3 normal. 410 g. per liter.

Ether, saturated with 6 normal HCl.

Sodium thiosulfate, 10 percent.

Sodium bicarbonate (solid).

### Preparing Unknowns.

The unknowns should contain 1 to 10 mg. per ml. of the constituent being sought, when solutions are given out for analysis. With solid unknowns it is more difficult to regulate the amount of an ion given, but the student should first analyze a 25 mg. sample, followed by a larger sample if traces of certain elements are suspected.

Satisfactory unknowns of the ferro-alloy type may be prepared by dissolving salts of the various elements sought ( $WO_4^-$ ,  $SiO_3^-$ ,  $VO_3^-$ , etc.) in a strongly acidified solution; iron is added to give a concentration of 100 mg.  $Fe^{+++}$  per ml., as contrasted with 1 to 2 mg. per ml. of the other ions. In this way a variety of samples may be secured which might be difficult to obtain as solids.

\* Impregnate filter paper strips with a solution of 4 g.  $K_3Co(CN)_6$  and 1 g. KCl in 100 ml. water.



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